# SOIL SCIENCE

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# SOIL SCIENCE

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# MINOR ELEMENTS

## EVIDENCE AND CONCEPTS ON FUNCTIONS, DEFICIENCIES, AND EXCESSES

There was a time when "C. Hopk'n's CaFe, Mg" (mighty good) adequately expressed our concept of the nutritive requirements of plants. Within the last quarter century, however, evidence of the need of a considerable number of other elements has increased to the point where the term "minor elements" has had to be introduced into the literature of plants and soils.

The number of elements included in the "minor" group continues to grow. In making up the list to be considered in this symposium, it was decided to include not only those most commonly mentioned, such as boron, manganese, copper, and zinc, but a considerable number of others that, when present in soils, may affect not only the well-being of plants growing on these soils, but of animals consuming the plants as well. Among this group are sodium, aluminum, selenium, cobalt, and molybdenum. Included also are iron and magnesium, elements that receive considerably less attention than do calcium, nitrogen, phosphorus, and potassium, which are the primary concern of the lime and fertilizer industries.

It is the hope of the editors of SOIL SCIENCE that these papers, all of them prepared by invitation, will serve a useful purpose by bringing together the points of view of a considerable number of specialists in this field of research. It is believed that many soil and plant scientists will find the summary of considerable value for reference purposes.

FIRMAN E. BEAR

# THE GEOCHEMICAL BACKGROUND OF MINOR-ELEMENT DISTRIBUTION

## V. M. GOLDSCHMIDT

*University of Oslo, Norway, Macaulay Institute for Soil Research, Aberdeen, Scotland*

### COSMIC FREQUENCY AND EVOLUTION

The distribution and the availability of the various chemical elements, including the "minor" elements, have been fundamentally controlled in broad outline by the chemical evolution of our planet during geological and pregeological time.

We may start with the consideration of the average chemical composition of matter in the universe (4, 6) as revealed by astrophysical investigations of stellar atmospheres, nebular masses, interstellar dispersed matter, and planetary atmospheres, and by chemical evidence on the composition of meteorites. The cosmic abundance of the chemical elements, or rather the various types of atomic nucleuses, is clearly dominated by general principles of nuclear stability and of nuclear evolution. By far the most abundant nucleus is the simplest one, the proton, of mass 1 and positive charge 1, the nucleus of the hydrogen atom. The transformation of protons into helium nucleuses, with mass 4 and charge 2, in the interior of stars, furnishes the main source of stellar energy. The stability of the various atomic nucleuses seems to be connected mainly with their mass number (weight), nucleuses with even mass number generally being more frequent than those with odd mass number, and nucleuses having a mass number which is a multiple of 4 being dominant up to a weight of about 60. Nucleuses having a higher weight than 60 are generally rare. The primary cosmic abundance of nucleuses has been modified by some subsequent processes of evolution, or rather decay, especially through the collisional instability of certain light nucleuses (including the elements lithium, beryllium, boron) under stellar conditions, by the decay of radioactive nucleuses, and probably also by processes of nuclear fission.

### PLANETARY EVOLUTION OF THE EARTH; PRIMORDIAL DIFFERENTIATION

Important processes of physical and chemical segregation and concentration dominate the history of matter during geochemical evolution, according to the properties not of the nucleuses but of the electronic shells of the various elements.

During the first, pregeological, evolution of our own planet, originally gaseous matter undoubtedly differentiated into certain condensed phases, presumably liquid, and into a residual gaseous phase, the primordial atmosphere.

This primordial atmosphere contained the most volatile, atmophile, elements, such as hydrogen, nitrogen, and the inert gases, as well as such compounds as water vapor and volatile compounds of carbon. The condensed phases, like those of meteorites, included a silicate slag which later provided the stony silicate mantle of the earth. Undoubtedly there was also a phase consisting mainly of metallic iron, and presumably there was also a phase consisting mainly of iron

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sulfide. We do not know for certain to what extent the present hydrosphere and atmosphere of the earth are direct differentiates of our primoridal atmosphere, but probably much of the primordial atmosphere was lost at the initially high temperatures by dissipation into cosmic space, while much gaseous matter has subsequently been contributed from the degassing of the lithosphere. Most important processes of atmospheric evolution are connected with biochemical processes, but certain chemical aspects of the primordial atmosphere are still seen preserved in the chemistry of ocean water, *e.g.*, the ample presence of chlorine, bromine, iodine, boron, and sulfur compounds, as compared to the scarcity of these elements in the lithosphere.

During the primoridal stages of differentiation of our globe, the distribution of the various chemical elements was thus essentially controlled by their chemical affinities toward oxygen and sulfur and by their latent heat of vaporization, especially in comparison with the corresponding affinities of iron, iron being the most common heavy metal in terrestrial matter.

As a suitable measure of these affinities we can take the free energy of oxidation per gram atom of oxygen of the lowest oxides of the electropositive elements, and the corresponding data for their compounds with sulfur. If we reckon these thermodynamic data from standard states, then that in itself involves the comparison with the relative ease of formation of condensed metallic phases.

Elements which have a higher free energy of oxidation than iron (for the lowest oxides involved), the lithophile elements, may be expected to concentrate in the silicate crust, the lithosphere, of the earth, during primordial differentiation. Such elements are, for instance, silicon, aluminum, alkali and alkaline earth metals. On the other hand, elements to be expected preferentially in the metallic iron phase are, for instance, nickel, cobalt, the platinum metals, and gold, which are siderophile elements. A few data may explain these relationships:

Free energy of oxidation from standard states in kilogram-calories per gram atom of oxygen $(-\Delta F°)$: CaO 144.3, $Al_2O_3$ 131.6, $SiO_2$ 96.0, MnO 91.2, $Na_2O$ 91.0, FeO 59.4, CoO 51.2, NiO 48.2, platinum metals 5 to 20.

A classification of the elements according to the free energy of sulfide formation from standard states, as compared with the formation of oxysalts, such as carbonates, gives the following sequence of affinities under the usual conditions of formation of sulfide ores in the lithosphere and characterizes chalcophile elements: Ag > Cu > Pb > Cd > Zn > Co > Fe > Ca > Mn, to mention a few examples.

From the thermochemical data we can thus understand the main trends in the primordial separation of the chemical elements, as regulated by the properties of the electronic shells of their atoms and ions.

### FRACTIONAL CRYSTALLIZATION OF SILICATE MAGMAS, IONIC RADII

The next main step in geochemical evolution is connected with the subsequent cooling of the earth and thereby the crystallization of the silicate slag, or the lithosphere of the earth, comprising the fractional crystallization of the bulk of

the silicate magmas. Processes of that type are still proceeding in formation of rocks from the plutonic and volcanic magmas of our own time.

The process of crystallization involves a sorting or selection of the various atoms, or rather ions, according to their size, with regard to their faculty for entering the crystal lattices or spatial networks of the different minerals, which crystallize from magmatic solutions. These minerals are mostly formed of negatively charged packings of silicate and aluminosilicate complex anions, in some cases also including fluoride or hydroxyl anions, and the anions are neutralized and cemented by the positive charges of cations of the various metals. In this manner the major and the minor constituents of magmatic rocks find their location in minerals, elements being selected according to the size of their ions, which is conveniently measured in ångstrom units, each such unit being 1 cm. $\times$ $10^{-8}$. The size of the various ions or atoms in crystal structures can be measured very exactly by x-ray interference methods, and is usually expressed by sets of radii under standard conditions of crystal structure, for the ionic radii usually under the standard conditions of the sodium chloride lattice type, for atomic radii usually under the condition of close packed (12-coordinated) metal structures, such as those given in the tables of ionic radii published by Goldschmidt (1) and Pauling (5).

### ISOMORPHOUS SUBSTITUTION IN MINERALS OF IGNEOUS ROCKS

Generally the possibility of large-scale isomorphous substitution in minerals from magmas will be limited to such pairs of ions, the radii of which agree within a tolerance of 10–15 per cent of the larger radius of the pair. For instance, magnesium (0.78 A.) and ferrous iron (0.83 A.) freely replace each other in ionic crystals, but not magnesium and calcium (1.06 A.). Divalent manganese occupies an intermediate position between magnesium and calcium, having an ionic radius of 0.91 A. and entering into isomorphous substitution either for magnesium or, in many cases, for calcium. Sodium (0.98 A.) and potassium (1.33 A.) do not usually substitute each other over any considerable range of concentration at ordinary or medium temperatures.

At very elevated temperatures, however, near the melting points of the minerals involved, isomorphous substitutions can take place even in cases of difference up to 20–30 per cent of ionic radii, as in the case of sodium feldspar and potassium feldspar, and between magnesium and calcium in certain clinopyroxenes. By rapid cooling, such unusual isomorphous mixtures can be temporarily stabilized even at lower temperatures, but sooner or later a segregation or unmixing of their components takes place.

In such cases when different ions of similar size and of the same charge (valency) substitute each other during the crystallization of minerals from cooling igneous rocks, the sequence for entrance of the various ions into the crystal lattices is generally the sequence of decreasing bond strength. The electrostatic bond strength, in cases of identical electric charge, is inversely proportional to the squares of the interionic distances: thereby the smallest ion is bonded preferentially. Thus magnesium ions are bonded before the somewhat larger ferrous

ions, and these again in preference to the manganous ions. In those cases where electronic bonds are present besides ionic bonds, the integral sum of bond strength is decisive: therefore, nickel is concentrated in the earliest fractions of magnesium silicates from magmas, even though nickel and magnesium have virtually identical ionic radii; and chromium spinels crystallize before other spinellide minerals because of the contribution of electronic bonding in the minerals of trivalent chromium.

Ionic substitution in minerals from magmas takes place not only between ions of identical charges having similar radii, but also in a great number of cases where ions of similar radii but different charge are concerned. In such cases the ion with higher ionic charge is captured in the crystal lattice in preference to the ion which has a lower charge. A very well known example is the series of plagioclase feldspars which are characterized by the substitution of divalent calcium for univalent sodium. Another example is the substitution between univalent lithium and divalent magnesium in certain minerals of the mica group. In such cases the sequence of entrance into the crystals is again the sequence of bond strength, the highly charged ions being captured by the crystal lattice, the lower charged ions being admitted only when the supply of the normal lattice components is nearly exhausted.

Generally we can classify the minor elements with regard to their ionic radii corresponding to the most important stages of ionization or of valency. Such a classification provides an arrangement according to their host minerals, these having some main constituent of similar ionic radius as the minor elements associated in them. From residual solutions and from gaseous phases from magmas the minor elements also can form various separate minerals of their own.

Starting our classification with cations that have the largest radii, we begin with those which have a radius near that of potassium. The magmatic minerals which are the most important hosts for such ions are potash feldspar, the most important, then the various mica minerals, and in comparatively few, mostly volcanic, rocks, the feldspatoid mineral leucite.

Comparable to univalent potassium (1.33 A.) are the univalent ions of rubidium (1.49 A.), thallium (1.49 A.), cesium (1.65 A.); the divalent ions of europium (1.25 A.), samarium (1.27 A.), strontium (1.27 A.), lead (1.32 A.), barium (1.43 A.); and to some degree also the trivalent ions neodymium (1.15 A.), praseodymium (1.16 A.), cerium (1.18 A.), lanthanum (1.22 A.). Cesium can enter potash feldspar to only a very limited concentration; any excess must be accommodated into mica or into pollucite, in which it is freely associated with rubidium.

Comparable to divalent calcium (1.06 A.) are the univalent sodium (0.98 A.), the divalent cadmium (1.03 A.), and to a certain degree the divalent manganese (0.91 A.) and strontium (1.27 A.), most probably also the divalent ytterbium (1.1 A.), the trivalent ions of yttrium (1.06 A.), and all the trivalent lanthanide elements from lanthanum (1.22 A.) to lutetium (0.99 A.). Quadrivalent ions of similar size to calcium are cerium (1.02 A.), uranium (1.05 A.), and thorium (1.10 A.). The ions of trivalent thallium (1.05 A.) and bismuth (1.1 A.) also belong to the same size class, as do the ions of univalent silver (1.13 A.). Im-

portant host minerals in igneous rocks are plagioclase feldspars, augite, apatite, sphene, fluorite.

Comparable to divalent magnesium (0.78 A.) are, besides ferrous iron (0.83 A.), a great number of ions of minor elements. They are: univalent lithium (0.78 A.), divalent nickel (0.78 A.), cobalt (0.82 A.), zinc (0.83 A.), manganese (0.91 A.), trivalent scandium (0.83 A.), antimony (0.8 A.), indium (0.92 A.), quadrivalent tin (0.74 A.), lead (0.84 A.), zirconium (0.87 A.), hafnium (0.85 A.), tellurium (0.89 A.). Some overlapping in ionic size and with regard to isomorphous substitutions occurs toward the following group. The most important host minerals are olivines, pyroxenes, amphiboles, and biotite micas.

Comparable to trivalent iron (0.67 A.) are the trivalent ions of aluminum (0.57 A.), gallium (0.62 A.), chromium (0.64 A.), vanadium (0.65 A.), rhodium (0.68 A.), titanium (0.69 A.), manganese (0.70 A.); quadrivalent manganese (0.52 A.), vanadium (0.61 A.), titanium (0.64 A.), ruthenium (0.65 A.), iridium (0.66 A.), osmium (0.67 A.), molybdenum (0.68 A.), tungsten (0.68 A.); quinquevalent columbium (0.69 A.), tantalum (0.69 A.), antimony (0.6 A.). Important host minerals are magnetite, other iron ores, and a number of aluminosilicates.

Comparable to quadrivalent silicon (0.39 A.) are divalent beryllium (0.34 A.), quadrivalent germanium (0.41 A.), quinquevalent phosphorus (0.34 A.), and perhaps hexavalent molybdenum and tungsten. Trivalent aluminum and gallium can substitute to some extent for quadrivalent silicon. Important host minerals in this group are many silicates and aluminosilicates.

To a group of the smallest[1] electropositive atoms belong trivalent boron (0.20 A.), quadrivalent carbon (0.15 A.) and quinquevalent nitrogen (0.11 A.) in borates, carbonates, nitrates. Host minerals are carbonates, carbonato-silicates, borosilicates.

Among important anions in minerals may be mentioned univalent fluorine (1.33A.) hydroxyl (1.4–1.8 A.), and divalent oxygen (1.32 A.), which all belong to the same size class. Another size class of anions is represented by the univalent chlorine, bromine, iodine, the divalent negative sulfur, selenium and tellurium, with radii from 1.74 to 2.20 A.

The geochemical distribution of minor elements according to their radii and ionic charges in igneous rocks (3, 7, 8), therefore, illustrates the well-known rules of association, for instance, of chromium, nickel, cobalt, and scandium with ultrabasic igneous rocks; of iron, titanium, vanadium, and copper with basic and intermediate rocks; of germanium, beryllium, and the rare earth elements, uranium, thorium, potassium, rubidium, and cesium with more acid rocks and with products of residual solutions.

### WEATHERING AND THE CYCLE OF SEDIMENTS, IONIC POTENTIAL

The processes of weathering and the cycle of formation of sedimentary rocks (3) in many respects parallel the operations of a gigantic semiquantitative chemical analysis, involving large-scale chemical separations. We can discern a num-

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[1] The radii given for the fictive state of positive central ions in the anions of the oxyacids.

ber of steps of such operations characterized mainly according to the separation of the following products:

1. Insoluble residues such as sand or sandstone, with such resistant minerals as quartz and zircon;
2. Hydrolyzates such as bauxite, clay, and shales, with hydrated oxides and hydrosilicates of aluminum;
3. Oxidates such as many sedimentary iron and manganese ores, with oxides and hydroxides of trivalent iron and trivalent or quadrivalent manganese;
4. Reducents such as coal, bituminous sediments, sedimentary sulfides and sulfur;
5. Carbonates such as limestone and dolomite;
6. Evaporates containing such salts as chlorides, sulfates, and borates of alkali and alkaline earth metals, and also carbonates and, exceptionally, nitrates.

In group 1 we may find concentrations of relatively insoluble and hard, often also heavy, minerals such as ilmenite, rutile, tourmaline, monazite, garnets, also metallic gold and diamond. In group 2 we find the bulk of aluminum, gallium, titanium, zirconium, many of the ions of the magnesium group such as nickel, scandium, and tin, columbium, tantalum, antimony, and many of the rare earth metals, as well as adsorbed potassium, rubidium, and cesium. In group 3 not only are iron and manganese locally concentrated, often in very large amounts, but also phosphorus, vanadium, lead, zinc, antimony, arsenic,[2] germanium, selenium, molybdenum, and tungsten. In group 4, besides much iron, sulfur, and arsenic, we find copper, zinc, indium, and silver, and sometimes much vanadium. In group 5 we find, besides most of the calcium and magnesium, much strontium, barium, fluorine, and boron, and also rare earth elements. If we look for a general principle controlling the distribution of elements in the processes of weathering and in the sedimentary cycle, we find that the ionic potential dominates much of the observed differentiations and associations. The ionic potential, the quotient between ionic charge and ionic radius, *i.e.*, the electrical field strength at the surface of each ion, dominates the interactions between the ion and water molecules. If the potential is low (large ions with small charge), such ions are apt to be collected in the evaporates, so far as they are not absorbed in the hydrolyzates, because of their strong polarizability, as is the case with potassium, rubidium, and cesium increasingly in order of increasing radius. With regard to base-exchange phenomena in the hydrolyzates of soils, the similarity of the ionic radii of potassium (1.33 A.), ammonium (1.43 A.), and hydroxonium (about 1.4 A.) seems to be of special geochemical importance.

The various members of the sedimentary cycle are often precipitated in the same sediment, such as hydrolyzates and oxidates in many common clays and shales. Reversals in the sequence of sediments are not uncommon.

## OXIDATION AND REDUCTION

The distribution of many minor elements depends very much on their stage of oxidation. Iron, manganese, and cobalt are often immobilized as a result of

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[2] The precipitation of many poisonous substances, together with the oxidate sediments, is a most important geochemical process, contributing greatly to preventing ocean water from being fatally contaminated.

processes of oxidation; sulfur, selenium, arsenic, vanadium, chromium, molybdenum, and tungsten may be mobilized by oxidation to readily soluble complex anions, in accordance with the rules of ionic potential; also, uranium may be made more readily soluble by oxidation from the quadrivalent to the hexavalent stage. The differences in geochemical behavior of selenium and sulfur are mainly due to differences in oxidation potential. In the processes of oxidation and reduction important biochemical processes participate and often dominate.

Many special peculiarities in the geochemical distribution of minor elements are due to special biogeochemical processes; hence, the concentration of a great number of rare elements in forest litter and in forest humus, fossil examples of which we find preserved in the assemblage of many minor elements in coal ashes (2). Other minor elements owe their special mode of distribution to the circulation in the atmosphere and hydrosphere, *e.g.*, the often air-borne iodine.

The experience of modern geochemistry clearly demonstrates that the same rules are in control of the distribution of all elements, the dominating constituents of the earth as well as the minor elements, and that the processes of soil formation and the composition of soils form only a special, but very important, chapter of geochemistry.

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# THE OCCURRENCE OF MINERAL NUTRITIONAL DISEASES OF PLANTS AND ANIMALS IN THE UNITED STATES

KENNETH C. BEESON

*U. S. Plant, Soil, and Nutrition Laboratory*[1]

The recent increase in interest in the distribution of nutritional troubles in plants and animals is a natural sequence to the earlier work of diagnosing and classifying these troubles and their various symptoms. Ordinarily, the investigator in these fields is interested in more than a mere description of the disorders observed even though such disorders may resemble those within his own experience. He also frequently wants to visualize the geographic extent of the trouble, and this is best accomplished by reference to maps. The preparation of such maps is still a rather hazardous undertaking, for although there is abundant information concerning the occurrence of nutritional diseases which are traceable to soil characteristics in the United States, there are relatively few reports that give specific information that may be used in plotting the data on maps. With the information now available, an attempt has been made in this paper, therefore, to present only very generalized areas associated with mineral troubles in either plants or animals.

### SOURCE OF INFORMATION AND METHOD USED IN DELINEATING AREAS

Credit to the many investigators throughout the United States who have contributed data through published papers or by correspondence can be given only general acknowledgment, since space does not permit the publication of a bibliography. The sources of data used in locating the points or areas on the maps consisted largely of published papers and experiment station reports, but a substantial amount of information has been obtained, also, through correspondence with workers in the field and from personal observations of the author.

The county was usually used as the smallest unit in plotting the data for mineral deficiencies in plants, although whenever possible the location within the county was also taken into consideration. When all of the data for one mineral and one plant species were plotted, two additional factors were then taken into consideration in outlining the general area of deficiency; namely, the physiographic and soil characteristics of the areas, and the general distribution of the crop in question. These factors were of considerable importance because frequently the statement was encountered that a deficiency had been observed throughout a particular valley or wherever a certain crop was grown on soils with some characteristic property. It was thus possible to develop areas of a very generalized nature to give a clearer concept of the possible extent of these disturbances than has been obtained heretofore.

This generalized presentation of areas was not feasible in the case of animal troubles except for iodine deficiencies. The occurrences of troubles in animals

are not nearly so frequently recognized as they are in plants, and much less has been done in definitely diagnosing and classifying them. Only the points of reported occurrence, therefore, were plotted. In instances, particularly with some phosphorus-deficient areas, it is not possible to give any particular locations, and in these cases only the fact that the deficiencies may occur throughout certain areas is indicated (fig. 3). The goiter belt was not plotted from original data but was taken from the map published by McClendon.[2] Reports from the literature and from the experiment stations indicate that the area outlined is substantially correct for animals as well as for man.
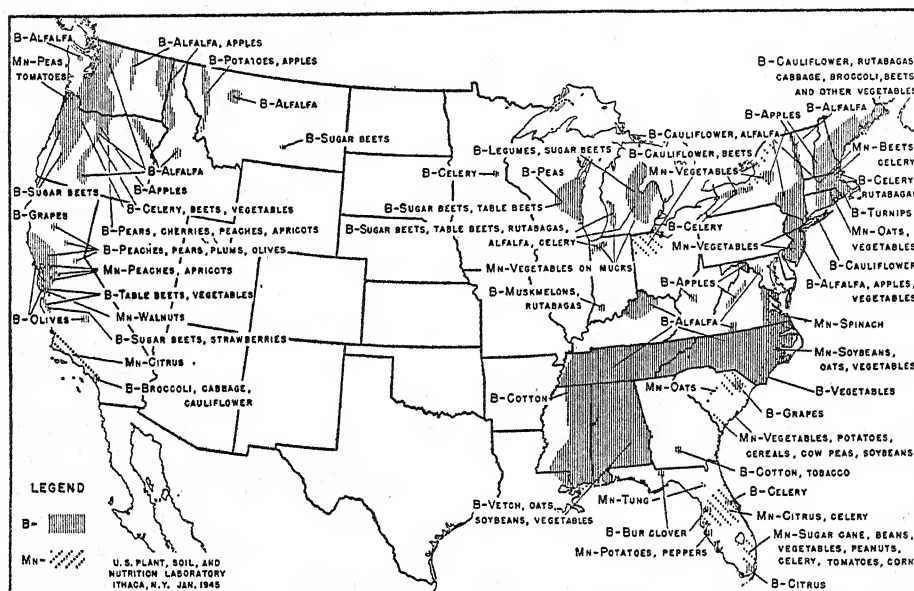


Fig. 1. Generalized Map of the Occurrence of Boron and Manganese Deficiencies in Plants

Although the deficient areas are necessarily shown as continuous, they are actually intermittent in character. Modification of these areas will be possible as more data become available.

## EXTENT OF TROUBLE AREAS

An examination of the area patterns on the maps (figs. 1 and 2) will suggest certain aspects of the distribution of troubles in plants:

1. There are some discontinuities in the patterns that might appear to be due to a lack of information or to an overemphasis of the extent of the deficiency. Either one or both factors may be important, for example, in the pattern for boron (fig. 1) in the Southeast. For certain crops, such as alfalfa, however, the states of Tennessee and North Carolina are considered to be almost entirely in the boron-deficient areas. Similarities of soil and

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[2] McClendon, J. F. 1927 The distribution of iodine with special reference to goiter. *Physiol. Rev.* 7: 189–258.

climate would suggest that South Carolina and Georgia should also be included in this area. Alfalfa, however, is not so important a crop in this region, and there is only slight evidence as yet that for any other crop these states can be generally classified as in the boron-deficient area. It is clear that the relationship between a mineral deficiency and a particular crop must always be taken into consideration.

2. The necessity for presenting a generalized picture of deficiency areas requires that poor regions within any area be treated as continuous. Thus, in the Southeast, pecans growing on the flood plains of the rivers seldom exhibit the typical zinc-deficiency symptoms,[3] whereas those growing on upland soils deficient in organic matter and excessively drained commonly have rosette.[4] Obviously, it would require a very large scale map to depict these differences.
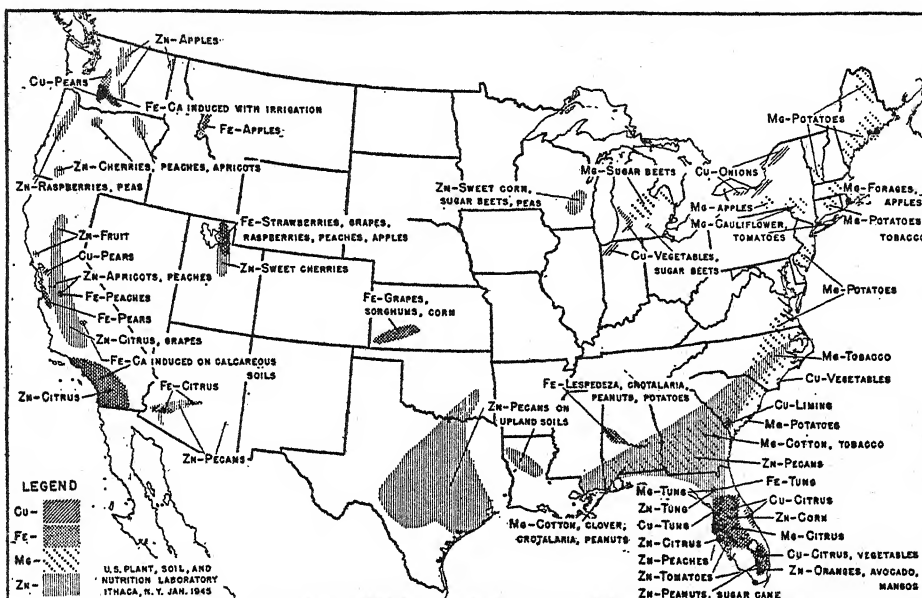


FIG. 2. GENERALIZED MAP OF THE OCCURRENCE OF COPPER, IRON, MAGNESIUM, AND ZINC DEFICIENCIES IN PLANTS

Although the deficient areas are necessarily shown as continuous, they are actually intermittent in character. Modification of these areas will be possible as more data become available.

3. The maps in figures 1 and 2 show deficiencies only in relation to certain crops. As has been pointed out, this should be kept clearly in mind in any consideration of the area patterns, for seldom do all or even any important part of all the crops grown in one area exhibit symptoms of the particular mineral deficiency associated with the designated crop. It has been repeatedly found, for example, that zinc in the pecan area of the Southeast is not limiting with respect to other crops growing in this region. Likewise, boron may be

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[3] McMurran, S. M. 1919 Pecan rosette in relation to soil deficiencies. U. S. Dept. Agr. Bul. 756.

[4] Demaree, J. B., Fowler, E. D., and Crane, H. L. 1934 Control of pecan rosette with zinc sulfate. *Proc. Ann. Conv. Southeast. Pecan Growers Assoc.* 1934: 29–37.
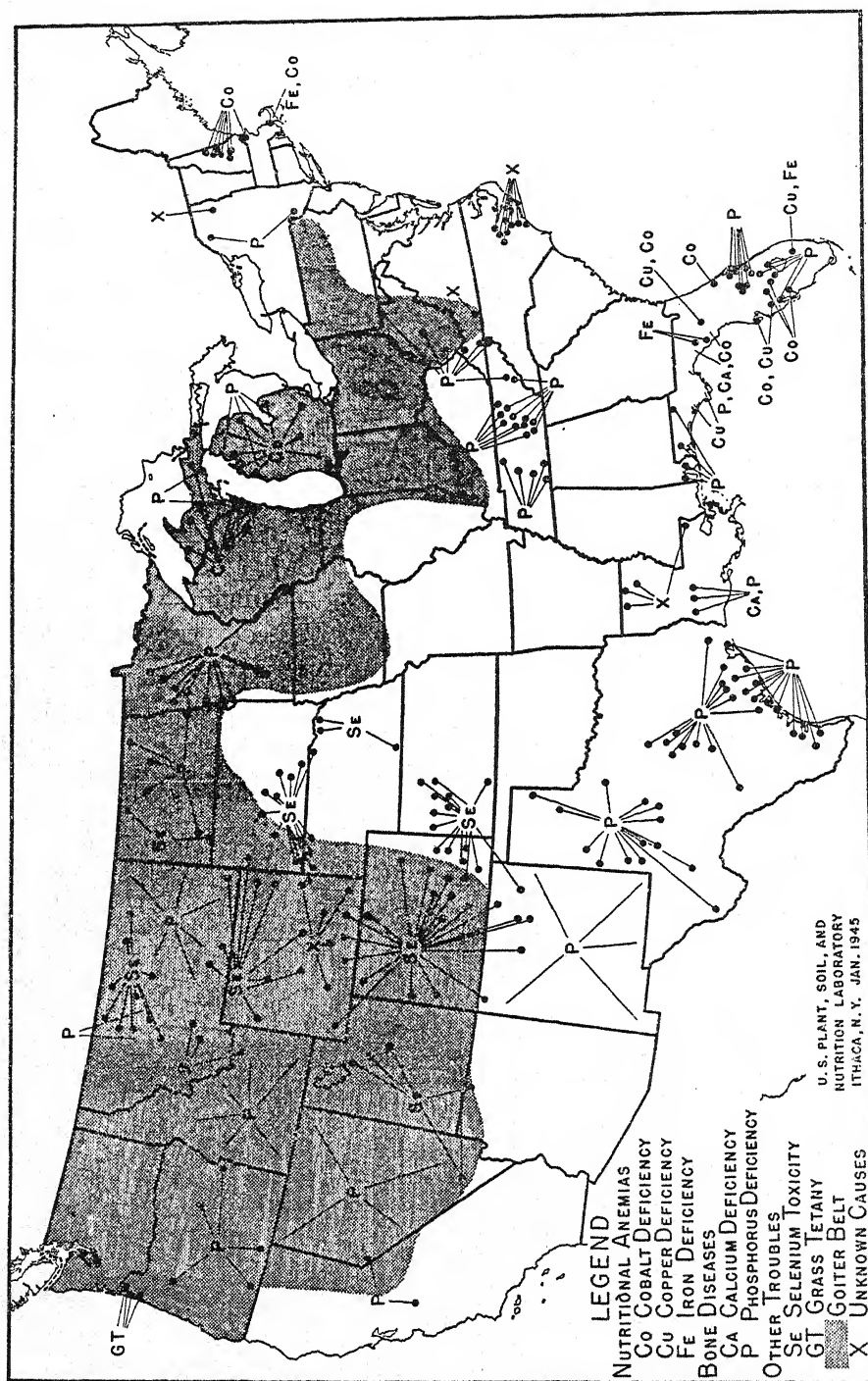
FIG. 3. OCCURRENCE OF MINERAL NUTRITIONAL DISEASES IN ANIMALS. The dots show the approximate location of the observed deficiency. The lines not terminating in dots indicate a generalized area where specific locations have not been reported. The goiter region is also a generalized area. As additional data become available generalized area patterns can be outlined for the other elements.

LEGEND

NUTRITIONAL ANEMIAS
Co COBALT DEFICIENCY
Cu COPPER DEFICIENCY
Fe IRON DEFICIENCY

BONE DISEASES
Ca CALCIUM DEFICIENCY
P PHOSPHORUS DEFICIENCY

OTHER TROUBLES
SE SELENIUM TOXICITY
GT GRASS TETANY
▨ GOITER BELT
X UNKNOWN CAUSES

U.S. PLANT, SOIL, AND
NUTRITION LABORATORY
ITHACA, N.Y. JAN. 1945

deficient with respect to apples, cauliflower, or certain legumes, although in the same fields, additions of this element may be of no value or actually detrimental to yields of other crops.

4. Although it is not the purpose of this paper to discuss causes for these deficiencies, it should be remembered that they are more frequently associated with liming practices than any other factor.

In general, it is clear that the highly leached, acid soils of the Coastal Plains and the podzol group are most frequently associated with deficiencies of the minor elements and phosphorus in both plants and animals. In the West there are extensive areas of alkaline soils that are also associated with deficiencies of these elements. Deficiencies of copper on mucks and other soils high in organic matter probably present special problems.

### RELATIVE IMPORTANCE OF THE VARIOUS TROUBLES

The most widespread deficiency in animals is, no doubt, phosphorus (fig. 3). Of the other deficiencies, none is widely known at the present time except that of iodine. It is of interest to note, however, the increase in the number of reports of observations of deficiencies in cobalt in the last 2 or 3 years. It appears possible, if these are further substantiated, that eventually cobalt-deficient areas may be defined over much of the Atlantic Coastal Plain and over the Northeast from Wisconsin through New England. It is highly probable, of course, that multiple deficiencies will be established eventually in many of these cases.

In the examination of experiment station reports and other published references to deficiencies in plants, the following numbers of reports for each element were encountered: boron 489, manganese 257, zinc 248, copper 189, magnesium 125, and iron 107. Not all of these reports cited deficiencies, because in many cases it was found that no benefit was derived from the use of these elements. It is believed, however, that the relative importance of deficiency troubles with respect both to the crops and the areas involved is substantially in this order at the present time.

### SUMMARY

Area patterns for the occurrence of nutritional troubles with respect to specific plant species and believed to be caused by deficiencies of boron, manganese, zinc, copper, or iron are presented for the United States. The occurrence of nutritional troubles in animals has been plotted with respect to the particular element—phosphorus, calcium, cobalt, copper, iron, iodine, or selenium—believed to be involved. Areas for the occurrence of nutritional diseases in animals cannot as yet be outlined, although more frequent and accurate diagnosis of both acute and subacute troubles will undoubtedly help in defining them more closely in the future.

# MINOR ELEMENTS IN PLANTS, AND SOME ACCUMULATOR[1] PLANTS

W. O. ROBINSON and GLEN EDGINGTON

*U. S. Department of Agriculture*[2]

Up to the present time approximately sixty elements have been positively identified in plants. Many of them, of course, are present in extremely small quantities. It would seem that all the known elements, excepting, perhaps, the rare or noble gases, could be found in plants, provided the analyst had enough plant material and employed sufficiently exhaustive and sensitive analytical methods. In this study we are concerned only with those minor elements that occur in plants in sufficient quantity to permit of fairly accurate quantitative determination.

Miller (26) gives a list of the elements found in plants. This list is repeated here with a few additions, including members of the rare earth group which have been announced since Miller's *Plant Physiology* was published. The major elements are not included. The elements, arranged in ascending order of atomic weights, are as follows: lithium, beryllium, boron, fluorine, sodium, aluminum, silicon, chlorine, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, yttrium, molybdenum, silver, tin, iodine, cesium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, eruopium, gadolinium, terbium, dysprosium, erbium, ytterbium, gold, mercury, thallium, lead, radium, thorium, and uranium. Some of these minor elements are present in exceedingly small quantities. Iodine, for instance, is measured in parts per billion, and the last three radioactive elements in the list would probably escape detection were it not for the very sensitive radioactive method.

In this study we are handicapped by the lack of sufficient data. For the purpose of determining whether there has been an accumulation it is desirable to know the normal or average quantity of a certain element in a variety of plants. The plant analyses made are naturally those of crop plants and have been generally confined to the elements used in fertilizers. Very little is known of the minor element composition of many plants and plant parts, such as tree leaves, mosses, shrubs, and wild grasses, that have modified the chemical composition of great areas of soils.

In this limited space we shall not consider accumulations by seaweeds or fungi.

The minor elements in plants may be divided roughly into two classes, essential and nonessential. There is much difference in opinion as to the particular elements in these classes, but if we take the minor elements more important agri-

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[1] The term "accumulation" is used here in the sense that certain plants take up the particular element in quantities very far above, sometimes many thousand times above, the average quantity for "normal" plants.

[2] Division of Soil and Fertilizer Investigations, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, Beltsville, Md.

culturally such as boron, manganese, iron, zinc, and copper, on the one hand, and such elements as titanium, barium, strontium, and lead on the other, we find that the effect of the first group on plants is fairly well known. Very little is known, however, about the effect of the second group on plant growth except in a few cases. Many of the second group are probably in the plant accidentally, and some may substitute for the more essential elements when these are present in insufficient quantities.

If we consider the minor elements which are most important from the agronomist's point of view; namely, boron, manganese, iron, zinc, and copper, there seem to be no very striking examples of crop plants' accumulating relatively large quantities of any except manganese. In a broad, general way, iron does not vary greatly in the green parts of plants. The same thing is true of the major essential elements. Among these major essential elements a tenfold variation is rare, whereas, in the case of manganese and silica, or better, aluminum and selenium and other nonessential elements, there are variations of a thousandfold or even a hundred-thousandfold.

A few of the most striking cases of food plants which accumulate minor elements are (a) the accumulation of 716 p.p.m. of manganese in the dry matter of pasture vegetation in certain acid soils of Sweden (33); (b) the accumulation of 14,950 p.p.m. of selenium in an astragalus plant that is sometimes eaten by cattle and from 45 to 155 p.p.m. of selenium in corn, peas, and wheat; and (c) the accumulation of as much as 4,030 p.p.m. of barium in Brazil nuts.

Very few plants are known which definitely accumulate large quantities of the minor elements. Some of these have been discovered recently, and nearly all have come to light as a result of a search for the cause of toxicity (barium and selenium) or as a result of other special properties, such as aluminum's being the cause of mordant properties of certain plants. The relatively few cases of plants accumulating relatively large quantities of minor elements with which we are familiar will be treated under the heading of the element accumulated.

## ALUMINUM

Hutchinson treats the biological aspect of aluminum fully in another chapter of this journal. Previous work by him (19) and others shows the sweet leaf, some of the club mosses, meadow beauty, shortia, galax, and hickory to be aluminum accumulators. Smith (31) cites a very striking case of aluminum accumulation in the Australian silky oak. In a cavity of one of these trees he found a large jelly-like deposit of basic aluminum succinate, and a part of the trunk farthest away from the deposit yielded an ash containing 79.61 per cent alumina. Much of our knowledge of aluminum-accumulating plants results from the early knowledge of dyeing cloth. Although most of these plants contained no coloring matter, the aluminum they contained served to set the colors generally furnished by other plants.

Table 1 gives the partial inorganic composition of the leaves of two high aluminum plants.

The data in table 1 shows that alumina is the main inorganic constituent of the leaves of the sweet leaf and of the whole plant of the princess pine. There

is over 50 per cent of alumina in the ash of the sweet leaf. Hutchinson and Wollack (20) quote an analysis by Von Faber of *Symplocos spicata* Roxb., showing 13.7 per cent $Al_2O_3$ in the dry plant. This appears to be the maximum for alumina in plants. There is a wide variation in the lime content of the two samples of sweet leaf growing near Raleigh, North Carolina. The analysis of the running pine is interesting because of its high alumina and very low lime. Analyses of this plant by Hutchinson and Wollack also show very low lime. High aluminum in plants does not necessarily mean low lime, as we have sometimes supposed. This is shown particularly well by the high lime in C 2554. The manganese in these plants, though comparatively high, is much lower than that in leaves of many trees growing on acid soils.

TABLE 1

*Partial inorganic composition of leaves of two high aluminum plants, dry weight basis*

| | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | MnO | CaO | MgO | $K_2O$ | $Na_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|
| | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent |
| Sweet leaf, *Symplocos tinctoria* | | | | | | | | | |
| C 6233 Near Gainesville, Fla., June | 7.67 | 0.09 | 0.014 | 0.050 | 1.76 | 1.25 | 2.02 | 0.30 | 0.33 |
| C 6902 Near Gainesville, Fla., Dec | 5.51 | 0.45 | 0.019 | 0.060 | 1.37 | 0.72 | 1.20 | 0.30 | 0.26 |
| C 2554 Lake Raleigh, N.C., June | 7.16 | 0.22 | 0.004 | .... | 2.44 | 1.22 | 1.64 | 0.10 | 0.30 |
| E 1483 Near Raleigh, N.C. | 5.77 | 0.03 | 0.021 | 0.097 | 0.67 | 0.87 | 1.41 | 0.16 | 0.25 |
| Princess pine, *Lycopodium flabelliforme* | | | | | | | | | |
| E 848 Falls Church, Va., Oct | 1.60 | 0.35 | 0.033 | 0.021 | 0.11 | 0.26 | 1.21 | 0.31 | 0.34 |

Table 2 shows the alumina and some other constituents of representative samples of hickory leaves from various localities.

The leaves of the hickory are not so high in alumina as those of the sweet leaf, and they show a tenfold variation. The alumina content varies in a general way with the acidity of the soil. The relation between these two factors is not a simple one, and probably other soil factors, such as variation in organic matter, particularly organic acids, which tend to hold alumina in solution, and the relative abundance of other ions, particularly calcium, affect the alumina content. There is a general tendency of calcium to vary inversely with the aluminum, but there are notable exceptions, such as C 7589 and C 2755. There is a very general tendency of the manganese to vary with the alumina.

Alumina in the ash of the hickory varies from about 3 to 37.5 per cent. A rapid test may be made for alumina in plant ash by leaching the ash with water and then gradually bringing the leachate to the neutral point with HCl. If alumina is present it forms a characteristic precipitate. This leaching process is

not quantitative, though it may be made to approach quantitativeness by fusing the residue with $K_2CO_3$ and leaching again.

### TABLE 2

*Inorganic composition of mature hickory and pecan leaves*
Dry-weight basis

| LAB. NO. | | $Al_2O_3$* | $SiO_2$ | $Fe_2O_3$ | MnO | CaO | MgO | $K_2O$ | $Na_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent |
| | *Hickory leaves* | | | | | | | | | |
| C 7611 | Near Chatham, Va. | 3.06 | 0.43 | 0.039 | 0.180 | 0.97 | 0.82 | 1.06 | 0.15 | 0.20 |
| E 847 | Meridian St., Falls Church, Va. | 2.71 | 0.28 | 0.034 | 0.490 | 2.25 | 1.12 | 0.87 | 0.11 | 0.20 |
| C 7587 | Near Beltsville, Md. | 2.67 | 0.38 | 0.020 | 0.570 | 1.33 | 0.52 | 1.31 | 0.17 | 0.40 |
| C 7582 | Near Rockville, Md., 2 inch tree | 2.13 | 0.35 | 0.055 | 0.370 | 2.54 | 1.14 | 0.94 | 0.16 | 0.32 |
| C 7583 | Near Rockville, Md., composite | 1.68 | 0.48 | 0.045 | 0.370 | 2.63 | 1.32 | 1.15 | 0.28 | 0.36 |
| C 7589 | Fisher's Gap, Skyline Drive, Va. | 1.59 | 0.14 | 0.009 | 0.317 | 3.59 | 0.66 | 0.82 | 0.12 | 0.36 |
| C 1602 | Big Savage Mt., Md.—1936, 5 inch tree | 1.55 | 0.13 | 0.020 | 0.478 | 2.20 | 0.60 | 1.07 | 0.14 | 0.53 |
| C 1603 | Big Savage Mt., Md.—1936 | 1.44 | 0.16 | 0.020 | 0.512 | 2.37 | 0.73 | 1.22 | 0.20 | 0.64 |
| C 755 | Big Savage Mt., Md.—1935, 5 inch tree | 1.31 | 0.14 | 0.020 | 0.439 | 1.97 | 0.46 | 1.22 | 0.15 | 0.30 |
| C 7601 | White Oak, N. C. | 1.33 | 0.47 | 0.152† | 0.350 | 2.95 | 0.89 | 1.42 | 0.21 | 0.26 |
| C 6901 | Gainesville, Fla. | 1.31 | 0.69 | 0.016 | 0.100 | 2.74 | 0.92 | 0.69 | 0.14 | 0.50 |
| C 2558 | Near Atkinson, N. C. | 1.24 | 0.73 | 0.010 | 0.055 | 3.00 | 0.86 | 0.95 | 0.19 | 0.33 |
| C 7588 | Jewell Hollow, Skyline Drive, Va. | 1.14 | 0.23 | 0.016 | 0.110 | 2.30 | 0.35 | 1.06 | 0.23 | 0.35 |
| C 7595 | Little Friar Mt., Va.—off vein | 0.79 | 0.09 | 0.007 | 0.120 | 2.52 | 0.45 | 1.14 | 0.24 | 0.39 |
| C 7593 | Little Friar Mt., Va.—vein | 0.60 | 0.24 | 0.011 | 0.100 | 2.82 | 0.70 | 1.58 | 0.22 | 0.42 |
| C 2755 | Moorefield Mine, Amelia, Va. | 0.72 | 0.22 | 0.039 | 0.179 | 2.16 | 1.08 | 1.22 | 0.10 | 0.37 |
| C 9014 | Luray Caverns, Luray, Va. | 0.63 | 0.39 | 0.018 | 0.558 | 3.42 | 1.02 | 0.92 | 0.19 | 0.29 |
| C 9026 | Overall, Va. | 0.47 | 0.14 | 0.020 | 0.176 | 3.48 | 0.78 | 0.88 | 0.19 | 0.27 |
| C 9050 | Lehigh, Iowa | 0.43 | 0.35 | 0.020 | 0.209 | 3.53 | 0.76 | 0.93 | 0.13 | 0.46 |
| C 757 | Near Hagerstown, Md. | 0.30 | 0.25 | 0.021 | 0.180 | 3.72 | 0.96 | 1.00 | 0.13 | 0.42 |
| | *Pecan leaves* | | | | | | | | | |
| E 1182 | Clemson, S. C. | 0.64 | 0.39 | 0.050 | 0.139 | 2.24 | 0.66 | 1.24 | 0.23 | 0.52 |

\* Includes also rare earths to the extent of a few parts per million in the lower $Al_2O_3$ percentages, but reaching as high as 2,000 p. p. m. occasionally in the very high $Al_2O_3$ percentages. Pecan leaves contained 100+ p.p.m. rare earths.

† High iron due to contamination with soil dust.

The pecan is closely related botanically to the hickory, and the one analysis of pecan leaves indicates that the pecan is an aluminum accumulator. The

alumina content of other samples may be more or less. The sample in table 2 contains about 7 per cent on the ash basis. It is not known what alumina content hickories would have when grown on the same soil as the pecan leaves. It is probable that leaves of cultivated pecans would be lower in alumina than leaves of uncultivated pecans grown where leaf mold is allowed to accumulate.

Stoklasa (32) and others have assumed that vegetation in the carboniferous era was high in alumina. One of the reasons given for this assumption is that coal ashes are high in alumina. As we now view it, this does not seem to be good evidence. The decaying part of plants contains very active absorption complexes which fix strongly such elements as iron and aluminum, and these elements are absorbed from the diffusing and percolating waters, displacing the more loosely held potassium and calcium.

## ARSENIC

It is reasonable to suppose that arsenic would be present in plants because it closely resembles phosphorus, which is essential to plant growth. The quantities of arsenic found in plants are generally small, however, and for the most part, plants will die before they accumulate as much as 10 p.p.m. Fellenberg (12) reports the case of a meadow soil so high in arsenic (1,580 p.p.m.) that it was not profitable to raise crops there. The scanty natural vegetation was so high in arsenic that it was said to be toxic to sheep, though it did not exceed 3.4 p.p.m. Areas dusted or sprayed with lead arsenate for the control of insects and areas sprayed with sodium arsenate for weed control have yielded some data on the arsenic content of plants. Thus, Williams and Whetstone (39) report instances of onions, radishes, and lettuce growing on soils receiving a heavy application of lead arsenate taking up from 6.5 to 1.9 p.p.m. arsenic on the fresh weight basis. The arsenic content on the dry-weight basis would be nearly ten times as much. Machlis (25) reports quantities up to 24.1 p.p.m. in leaves of the Macadamia nut tree where sodium arsenite had been used for weed control.

There is a possibility that some arsenic-accumulator plants may have escaped detection because the arsenic may be in an organic form difficult to break up by the Kjeldahl digestion, which is commonly employed.

## BARIUM

Seaber (30) and later Wagner (36) have reported a very interesting case of barium accumulation by the Brazil nut. Seaber's attention was directed to the problem by the fact that some children were made ill by a Brazil nut confection. He separated as much as 3,100 p.p.m. of barium from the nuts. He found that all Brazil nuts contained barium, though in variable quantities. Brazil nuts from certain localities were much higher in barium than those from other localities, indicating a soil difference. It would be interesting to learn the barium content of the leaves of the Brazil nut tree. Since there is but little calcium in seeds, this instance of barium accumulation seems remarkable. We have found as high as 4,030 p.p.m. of barium in the analyses of a number of Brazil nuts purchased on the Washington market. Most samples contain less, but all contain a considerable quantity of barium. Strontium is also present in the Brazil nut in amounts greater than traces.

## BORON

Cook (9) reported 283 p.p.m. boron in cowpeas (part above ground) grown in Florida, and 152 p.p.m. in radish roots grown in the same state. These values are very much higher than the other boron determinations given by Beeson (5), but since the boron analyses given by Cook of other plants are within the common ranges, it seems that Cook's high values should stand. McHargue, Hodgkiss, and Offutt (24) found 150 p.p.m. boron in hickory leaves.

As a rule, boron does not exceed 70 p.p.m. in naturally grown plants leaves. Plants growing in saline soils in which there is comparatively much boron, however, will take up much larger quantities of boron. Under these conditions the boron is generally toxic. Eaton (11) grew a large variety of plants outdoors in sand cultures to which varying quantities of boron had been added. The toxic limit was reached in almost all cases, but there were great differences in boron content of the different kinds of plants. The nutrient solutions contained boron in much higher concentrations than ordinary soils, and the boron contents are consequently much higher than in naturally grown plants. It may be that the plants which had the highest boron contents under these conditions would tend to have high contents under natural conditions. Eaton reports 3,875 p.p.m. boron in muskmelon, 3,080 in zinnia, and 2,245 in sweet clover. All determinations are on the leaves. Although these results are much higher than those previously reported, the analytical work is unquestionably reliable.

## COBALT

Cobalt is mentioned here because of its importance to animal nutrition. It is taken up very sparingly by plants. Askew and Dixon (1) report 4.6 p.p.m. Co in a specimen of white clover from Australia.

## COPPER

Verodi (35) in 1896 reported wheat grains to contain as much as 710 p.p.m. copper, and pepper pods 1,350 p.p.m. These values are so divergent from so many other values that they do not seem reliable. Heckel (16) found 560 p.p.m. Cu in *Polycarpia spirostylis* which grew in Australia on a high copper soil. Lehmann (22) found in *Thymus serpyllum* 223 p.p.m. Cu, in dandelion 320 p.p.m., in *Viola hirto* stems 560 p.p.m., all growing in soil having 0.271 to 0.349 p.p.m. Cu. Davidson and LeClerc (10) report various samples of spinach to contain from 28 to 73 p.p.m. Cu. Guerithault (15) found 17.1 p.p.m. Cu in oat grain but not more than 7.5 p.p.m. in wheat and other grains. This latter figure is mentioned because of Verodi's astonishingly high results given above. In this connection R. S. Holmes, of this Bureau, found a maximum of 7.5 p.p.m. Cu in 25 samples of wheat grains from the Great Plains and from Portugal.

## FLUORINE

Despite the fact that fluorine is applied with fertilizers as superphosphate in rather liberal quantities for a minor element, very little fluorine appears to be taken up by plants. Gautier and Clausman (14) found 139 p.p.m. F in sorrel

and 134 and 85 p.p.m. in beet leaves and ferus, respectively. Bartholomew (3) found as high as 1,970 p.p.m. F in the roots of cowpeas grown in a water culture containing 10 p.p.m.

## IODINE

Iodine is mentioned here only because of its importance in animal nutrition. Beeson (5) cites analyses of turnips (whole plant) containing 95 p.p.m. I. These had been fertilized with salts containing iodine. Spinach likewise fertilized contained 49 p.p.m.

## MANGANESE

In certain pasture herbage growing on very acid soil in Sweden the MnO content exceeds 700 p.p.m. (33) in a few cases. This is the maximum we are aware of. Horses pastured or fed on this herbage developed a peculiar anemic condition. Beeson's tables (5) show that ordinary crop plants contain but a few hundredths or even but a few thousandths of 1 per cent. Bailey and Anderson (2) give tobacco analyses showing as high as 2,262 p.p.m. of manganese for certain plants grown in Connecticut. The leaves of a number of trees which are very tolerant of acid soils conditions may take up relatively large quantities of manganese, though the same trees growing on neutral or limestone soils may take up very little. Table 2 shows the very variable manganous oxide content of hickory leaves, which vary from 0.055 to 0.570 per cent, or on the ash basis, from 0.5 to 6.1 per cent. These larger percentages correspond more nearly to those of a major rather than a minor element in plant composition.

Exchangeable manganese in the organic layers of podzol soils sometimes equals and occasionally exceeds the exchangeable calcium. High manganese must be the rule in the composition of the leaves supplying the organic matter.

## MOLYBDENUM

Ferguson *et al.* (13) have reported an interesting case of clover pasturage in Somerset, England, taking up as much as 100 p.p.m. of molybdenum. Apparently, molybdenum is taken up more readily from soils limed to alkalinity than from acid soils. Beath (4) reports that in parts of Wyoming the woody aster has been found with 221 p.p.m. of molybdenum, and the devil's paint brush with 333 p.p.m. These accumulations are far greater than any observed up to very recent times. Ter Mulen (34) found 9.1 p.p.m. Mo in the seeds of the chick-pea. Other plants and plant parts contained considerably less.

## RARE EARTHS

By rare earths we mean that analytical group having insoluble hydroxides, fluorides, and oxalates. Specifically, it includes the elements, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europum, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. We have found an interesting case of the accumulation of rare earths by hickory trees, and Milton, Murata, and Knechtel (27) discovered that chestnut leaves concentrate rare earths.

A comparatively few localities where hickory trees grow have been investigated by analyzing the hickory leaves for rare earths. At present we believe this gives what might be called the "hickory rare earth index" of the particular soil growing the trees. This term indicates the rare earth content, in parts per million, of mature hickory leaves grown under conditions in which the dead leaves are not removed. Incomplete data indicate that various hickories grown on the same soil produce leaves of similar rare earth content. Table 3 shows the rare earth content of hickory leaves from various localities arranged in order of quantities present. In some cases the rare earth content of leaves gathered in June or July must be given. These are not comparable with mature leaves gathered at the last of the season. Mature leaves seem to contain two to three times as much rare earths as leaves gathered early in the season.

The rare earth determinations were made on large samples, generally 100 gm. dry matter. The rare earths were first precipitated with an excess of ammonia, phosphorus was removed, and most of the alumina was separated by its solubility in 10 per cent sodium hydroxide followed by an ammonia precipitation. The rare earths were then separated from the iron, alumina, etc., by two oxalate separations. The method gives somewhat low results. Recoveries up to 90 per cent have been made on additions corresponding to 200 p.p.m. The method is sufficiently sensitive, however, to detect rare earths in almost any variety of leaves growing in localities where hickory leaves contain more than 500 p.p.m.

A few generalizations seem to be warranted by the data. There are four rather definite areas that produce hickory leaves high in rare earths. These are the vicinities of Rockville, Maryland; White Oak, North Carolina; Falls Church, Virginia; and Amelia, Virginia. Of these areas only the Amelia, Virginia, locality was definitely known to produce rare earth minerals (allanite, microlite, tantalite). The soils of the high rare earth areas are residual from granite or gneiss. The data from the Friars Mountain area indicate that leaves from hickory trees but a short distance apart may vary considerably in rare earth content. The tree off the vein of allanite was less than 150 yards below the vein and mine dump and to one side of the vale on a steep hillside. The soil was very shallow over an uneven rocky surface. On the other hand, the data on the deep soils of Rockville, of White Oak, and, in general, of Falls Church, indicate comparatively little variation of hickory tree leaves growing near together.

The distribution of rare earths in parts of the hickory tree is interesting. Two cases follow:

Rare earths (p.p.m.) in parts of a small hickory, Moorefield Mine, Amelia, Virginia

| | |
|---|---|
| Small twigs | 50 |
| Wood of trunk | 40 |
| Wood of taproot | 57 |
| Bark of taproot | 140 |

Rare earths (p.p.m.) in fruit of hickory tree No. 3, Falls Church, Virginia

| | |
|---|---|
| Nut meats | 5 |
| Nut shells | 7 |
| Nut husks | 17 |
| Tree leaves | 981 |

Only one analysis of pecan leaves for rare earths is available. This sample[3] was grown at Clemson, South Carolina, and contained 100 p.p.m. of rare earths.

TABLE 3
*Rare earth content of hickory leaves**
Dry weight basis

| | RARE EARTHS | | RARE EARTHS |
|---|---|---|---|
| | *p.p.m.* | | *p.p.m.* |
| Near Rockville, Md., 1935 | 2106 | Edgewood Arsenal, Md. | 295 |
| Near Rockville, Md., 1940 | 2148 | Antietam, Md. | 286 |
| Near Rockville, Md., 1940 composite | 2296 | Bessemer City, N. C., June | 275 |
| Near Rockville, Md., 1944 composite | 2200 | Blacksburg, Va. | 270 |
| Meridian St., Falls Church, Va. | 1513 | Hopkinton, Conn. | 232 |
| Durwood, Md. | 1296 | Near College Park, Md., June | 196 |
| White Oak, N. C., large tree, June | 880 | Blackford, Va., June | 195 |
| White Oak, N. C., large tree, Sept. | 1248 | White Plains, N. Y., July | 193 |
| White Oak, N. C., composite, June | 1012 | Near Criglersville, Va., June | 190 |
| White Oak, N. C., composite, Sept. | 1326 | Near Hagerstown, Md. | 176 |
| Oak St., Falls Church, Va., tree No. 1. | 759 | Near Raleigh, N. C., June | 154 |
| Oak St., Falls Church, Va., tree No. 2. | 1056 | Near Chatham, Va. | 139 |
| Oak St., Falls Church, Va., tree No. 3. | 759 | Hiddenite, N. C., June | 133 |
| Oak St., Falls Church, Va., tree No. 4. | 1061 | Marlboro, N. H., July | 124 |
| Oak St., Falls Church, Va., tree No. 5. | 784 | Bethany, S. C., June | 110 |
| Oak St., Falls Church, Va., tree No. 3, June 1 | 174 | Near Norbeck, Md. | 100 |
| | | Luray, Va. | 96 |
| Oak St., Falls Church, Va., tree No. 3, July 4 | 634 | Atkinson, N. C., June | 95 |
| | | Newington, Conn., July | 67 |
| Oak St., Falls Church, Va., tree No. 3, Oct. 1 | 981 | Spruce Pine, N. C., June | 67 |
| Near Amelia, Va., July | 726 | Lehigh, Ia. | 54 |
| Near Amelia, Va., July | 781 | Overall, Va. | 54 |
| Near Amelia, Va., Aug. | 858 | Piney River, Va. | 48 |
| Near Amelia, Va., Aug. | 1155 | Hall, Md. | 46 |
| Near Beltsville, Md., 1941 | 784 | Glenville, Conn., July | 37 |
| Near Beltsville, Md., 1942 | 713 | Waterloo, Ia., June | 28 |
| Jewell Hollow, Skyline Drive, Va. | 685 | Winchester Mt., July | 17 |
| Friars Mt., Va., June | 341 | Frostburg, Md. | 11 |
| Friars Mt., Va., Sept. | 601 | Hunting Hill, Md. | 6 |
| Friars Mt., Va., Sept. | 559 | Dublin, Md., June | 3 |
| Friars Mt., Va., off vein | 96 | Gainesville, Fla., June | 2 |
| Fisher's Gap, Skyline Drive, Va. | 572 | Gainesville, Fla., Dec. | 10 |
| Largo, Md. | 490 | | |
| Near Criglersville, Va., June | 412 | | |
| Attleboro, Mass. | 308 | | |

* Mature leaves, unless otherwise indicated.

The pecan and hickory are so closely related botanically that the pecan might be expected to be a rare-earth accumulator. As no data are available on the rare earth content of hickory leaves from this locality, comparisons are not possible.

[3] Kindly furnished by A. M. Musser.

So far as is now known, the hickory greatly exceeds other plants in rare earth accumulation. Milton *et al.* (27) found 0.06 per cent of rare earths in dry leaves of chestnuts growing near Vesuvius, Virginia. We found 65 p.p.m. in leaves of diseased chestnut sprouts in July at Falls Church where the hickory rare earth index for that time is about 650. Chestnut leaves near College Park contained 18 p.p.m., and hickory leaves there, 196 p.p.m. Mature chestnut leaves in the high rare earth Rockville area contained 433 p.p.m. In the Falls Church area with a hickory rare earth index of about 800, rhubarb stalks and leaves took up 100 p.p.m. of rare earths. At the Moorefield Mine area near Amelia, Virginia, with a hickory rare earth index about 800, a sample of pine needles contained 149 p.p.m.

It was at first suspected that aluminum accumulators might be also rare earth accumulators. Hutchinson and Wollack (20) found no rare earths in a sample of running pine. which is a very notable aluminum accumulator. However despite the fact that the hickory rare earth index of the soil growing the running pine was only 15, they concluded that aluminum accumulators are not necessarily rare earth accumulators. We have recently confirmed Hutchinson and Wollack's conclusions. A large sample of running pine was gathered under a sizable hickory tree growing in Falls Church, Meridian Street locality. The leaves of the hickory tree contained 1,513 p.p.m. of rare earths (item 5, table 3). The underground stems of the running pine permeated the leaf mold, which appeared to be formed largely from the hickory leaves, and it would seem that the running pine would take up rare earths under these conditions if it ever does. However, there was less than 4 p.p.m. of rare earths in the running pine. That is, a precipitate of crude rare earths of 0.4 mgm. was obtained from 100 gm. of the dry matter, and probably only a part of this crude precipitate was actually rare earths. Furthermore, two samples of sweet leaf recently analyzed yielded crude rare earth precipitates of 7 and 9 p.p.m. Since the sweet leaf is a most notable alumina accumulator we conclude with Hutchinson and Wollack that it would "appear that a high concentration of alumina by no means necessarily implies a concomitant concentration of the rare earth elements."

## SELENIUM

The variation in the selenium content of plants seems to exceed that of any other element. The extreme variation is between the limits of less than 0.1 to 14,900 p.p.m. in the *Astragalus racemosus* observed by Beath (4), a 149,000-fold variation or more.

The selenium content of a number of plants very high in this element is given in table 4. All these plants are notable selenium accumulators. The selenium content of the soils of the localities given in table 4 is not necessarily very high. Other plants growing on the same soil may take up only a trace of selenium. This point is well brought out by Williams (37), whose data are reproduced in table 5.

The data in table 5 show decisively that different plants accumulate very different amounts of selenium when growing on the same soil. There is a 4,000

to 1 ratio between the highest and the lowest content, showing great selective powers for selenium on the one side and, perhaps, rejective powers on the other.

Selenium enters into the compositions of various grains and other food plants. Wheat and corn grain take up as much as 45 p.p.m. Se when grown on some high selenium soils of South Dakota [Williams *et al.* (40)]. We have recently found as high as 110 p.p.m. Se in peas and 155 p.p.m. in wheat grown in Colombia,

TABLE 4

*Selenium content of certain plants very high in selenium*

Plant above ground, dry-weight basis

|  | SELENIUM |
|---|---|
|  | *p.p.m.* |
| *Astragalus racemosus*, Wyoming (21) | 14,900 |
| *Oonopsis condensata*, Albany Co., Wyoming (6) | 9,120 |
| *Astragalus bisulcatus*, Crook Co., Wyoming (7) | 6,530 |
| *Astragalus racemosus*, Dawes Co., Nebraska (7) | 5,560 |
| *Xylorhiza parri*, Albany Co., Wyoming (6) | 5,390 |
| *Astragalus pectinatus*, Teton Co., Montana (38) | 5,170 |
| *Astragalus racemosus*, Gregory Co., South Dakota (28) | 4,800 |
| *Astragalus grayii*, Carbon Co., Wyoming (6) | 4,450 |
| *Aplopappus fromontii*, Huerfano Co., Colorado (8) | 4,320 |
| *Stanleya pinnata* or *bipannata*, Pueblo Co., Colorado (8) | 1,390 |

TABLE 5

*Selenium content of various plants collected simultaneously from the vegetative growth on gritty clay loam containing 2 p.p.m. Se, Kiowa Co., Colorado**

|  | SELENIUM |  | SELENIUM |
|---|---|---|---|
|  | *p.p.m.* |  | *p.p.m.* |
| *Astragalus pectinatus* | 4000 | *Xanthium* sp. | 6 |
| *Stanleya pinnata* | 330 | *Salsola pestifer* | 5 |
| *Aplopappus fremontii* | 320 | *Munroa squarrosa* | 4 |
| *Gutierrezia sarothrae* | 70 | *Helianthus annuus* | 2 |
| *Lea mays* | 10 | *Bouteloua gracilis* | 2 |
| *Euphorbia* sp. | 10 | *Malvastrum coccineum* | 1 |

* After Williams (37).

South America. Hurd-Karrer (18) reports that cabbage leaves raised in the greenhouse on selenated soils take up as much as 758 p.p.m. Se.

### SILICON

A number of plants furnish clear cases of silica accumulation. Wolff's ash tables show many cases of silica accumulation, and the high silica content of various grasses is so well known it hardly needs discussion here. However, we have a very clear case of accumulation among the grasses and in other plants. The soil is very high in silicon. It is, in fact, next to oxygen, the most abundant

element in soils in general, and silicon is comparatively abundant in the soil solution, yet for the most part, silicon is rejected by plants. Some of the scouring rushes contain over 70 per cent silica in the ash, and in the ash of cereal straws there is frequently over 50 per cent. We have recently found over 60 per cent silica in the ash of the viper's bugloss. Doubtless, many other plants will be found high in silica.

## VANADIUM

Vanadium resembles phosphorus and is present in considerable quantities in clays and soils. Beath (4) cites examples of supposed vanadium and uranium concentrations by plant life, but he speculates that these elements have been concentrated by the organic matter of plant remains rather than by the growing plant. Some Peruvian shales contain up to 0.5 per cent $V_2O_5$. It is thought by some that this concentration has been effected biologically. A considerable source of vanadium has been the flue dust of ships burning Venezuelan oil. The ash of certain asphalt products ranges between 35 and 40 per cent $V_2O_5$, though the total ash is low. It is supposed that present in certain of the organic remains are compounds which have a great affinity for the merest traces of vanadium analogous to the affinity that dithiozone compounds have for the merest traces of some of the metals. Amounts of $V_2O_5$ of about 20 p.p.m. have been reported in clover, beets, beans, and pine needles.

## ZINC

There is the classical case of a certain violet, *Viola calaminaria*, taking up huge quantities of zinc from soils in the zinc industrial region of Belgium. In this case, however, there is some question of zinc dust contamination. Rogers, Gall, and Barnette (29) reported 714 p.p.m. zinc in Diodella and 585 p.p.m. in foxtail growing in Florida on a sandy soil in which corn showed a zinc deficiency. Lyman and Dean (23) found 144 and 158 p.p.m. zinc in the tips of the leaves of the pineapple plant. Hibbard (17) found 162, 187, and 208 p.p.m. in specimens of *Malva rotundifolia* grown in California. R. S. Holmes, of this Bureau, found that ragweed plants growing on a zinc mineral outcrop near Zinc, Arkansas, had accumulated 3,800 p.p.m. zinc. Lamb's quarters and prickly lettuce grown on the site of an old hogpen in Beltsville, Maryland, contained 600 and 512 p.p.m. zinc, respectively. Holmes also found that tobacco plants growing on an un-limed soil in a galvanized lysimeter tank took up as high as 1,540 and 2,000 p.p.m. of zinc as determined in the whole plant above ground. The fact that a plant may show a deficiency disease with respect to zinc does not necessarily indicate that such a plant is normally high in zinc. Pecan trees frequently show zinc deficiency, yet Holmes' data show many healthy pecan leaves to be rather low in zinc.

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# ALUMINUM IN SOILS, PLANTS, AND ANIMALS

G. EVELYN HUTCHINSON[1]

*Osborn Zoological Laboratory, Yale University*

Aluminum occupies a somewhat anomalous position among the biological elements, in that it is a very common and important constituent of the inorganic materials of the biosphere, but a rare and usually unimportant constituent of living matter itself. Both the importance of the element in the environment and its relative unimportance within the organism are ultimately to be referred to the dimensions and charge of the $Al^{+++}$ ion.

The radius of the aluminum in ionic crystals falls between that of the doubly charged magnesium and the quadruply charged silicon ion: $Mg^{++}$, $r = 0.78$; $Al^{+++}$, $0.57$; $Si^{++++}$, $0.39$. In the lattice structure of the aluminosilicate clay minerals, limited substitution of $Al^{+++}$ for $Si^{++++}$ or of $Mg^{++}$ for $Al^{+++}$ is possible. The base-exchange properties of the pedolites are now frequently interpreted in terms of the lack of electrostatic balance produced by such substitutions.

The relative unimportance of aluminum within the organism is doubtless due to the low solubility of the element in neutral solutions. Goldschmidt (14) has pointed out that, considering only those lithophil elements of essentially invariant valency, a diagram may be constructed in which the point occupied by the element is defined by its ionic radius and its valency (fig. 1).

Elements having a low ratio of charge to radius tend to form more or less soluble cations; elements having a high ratio form anions with oxygen. In the middle sector of the quadrant, in which Be, Al, Ti, Th, Zr, and Hf lie, the elements tend to form oxides insoluble in neutral water. The contours introduced into the diagram express the ratio of mean concentration within living plants to that in the accessible lithosphere and so indicate the importance of the relationship in determining biological availability. As the commonest of the elements occupying the middle sector of this diagram, the behavior of aluminum has a theoretical interest in biogeochemistry, while the definition of the conditions under which abnormal amounts of the element are present in the immediate

Since this article was written, a paper by B. B. Polynov [*Bull. Akad. Nauk. USSR, Ser. Geol.* 1944 (2) 3–14] has been received. The author notes considerable amounts of aluminum in all plants growing on alluvial red earth in the foothills of the Caucasus. *Carpinus betula* contained 8.5 per cent Al in the ash of the leaves, whereas in other parts of Europe only a trace is present. He regards aluminum accumulation as a region phenomenon dependent on climatically determined soil types; it is, however, clear that the vegetation of such regions consists of aluminum-tolerant species. Polynov also indicates that he has found that the lichen *Parmelia* promotes the decomposition of primary rocks; both $Al_2O_3$ and $SiO_2$ enter the plant body, and on subsequent death and decay, montmorillonite is formed.

environment of organisms is of great practical agricultural importance. The present review aims at summarizing the present state of knowledge of all the more interesting aspects, both theoretical and practical. Since the writer has recently published a longer discussion of the same subject (22), bibliographic citation to older work, now superseded or known to be erroneous, will not be given in the present contribution.
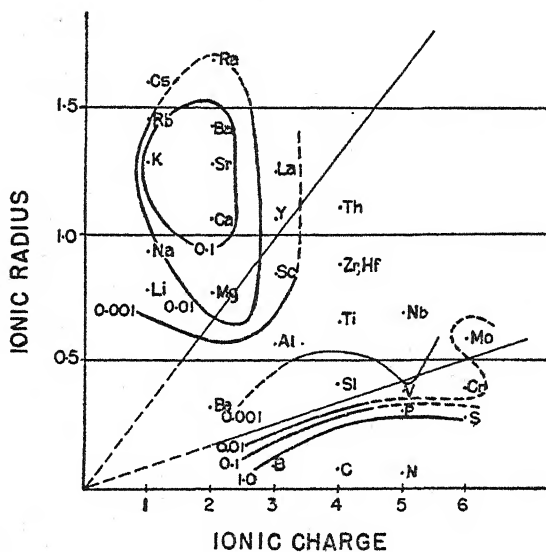


FIG. 1

ALUMINUM IN SOILS

Aluminum occurs in undecomposed rock fragments, in secondary alumino-silicate clays, as solid or hydrosol hydrated oxides, as phosphates, and in ionic form. The decomposition of rock fragments is a much-studied but inadequately understood process. Mechanical subdivision and the action of colloidal clays and organic matter may remove cations and so initiate decomposition. Carbon dioxide and organic acids have generally been regarded as important agents; the role of sulfuric acid has been somewhat neglected. The origin of alumina in soils may be attributed to such decomposition, or to the similar decomposition of secondary minerals. Vinogradov and Boichenko (67) have established that diatoms can decompose nacrite, and therefore biological action in liberating alumina has to be considered. The general trend of such changes has long been known to depend on climate, sesquioxides migrating downward in podzols of high-temperate latitudes, whereas silica is removed by leaching in the tropics. Even in low-temperate latitudes *gibbsite* $Al(OH)_3$ may constitute 30 per cent of the inorganic soil colloid (1).

The phosphate present in virgin soils varies considerably in availability and when relatively soluble phosphatic fertilizers are added to soils, the additional phosphate tends to become fixed in a more or less insoluble form. Fixation by

formation of aluminum and iron phosphates, and by aluminosilicate pedolites occurs, but in most cases the former process is of somewhat greater importance (6).

Little information exists as to the mineralogy of the aluminum phosphate in soils. Various attempts have been made to identify mineral phosphates by means of pH solubility curves. Stelly and Pierre (61), however, find that mixtures of apatite and vivianite cannot be satisfactorily distinguished from aluminum phosphates, nor can the two aluminum phosphates most likely to occur, namely, variscite, $AlPO_4 \cdot 2H_2O$, and wavellite, $Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$, be separated by their solubility minima, though the basic wavellite is somewhat more soluble under the conditions of their experiments. Their work, however, gives strong evidence for the existence of different mineral phosphates in different soils.

A great variety of complex aluminum phosphates is known from sedimentary rocks; some of these might be soil constituents. The clay-like minervites, supposed by Vernadsky (66) to be analogous to the aluminosilicate clays, deserve renewed investigation.

The occurrence of aluminum extracts of acid soils made with neutral salt solutions has been known at least from the observations of Veitch (65). Rice (45) showed that the element did not appear until the pH of the extract fell below 4.5. The whole question became of considerable practical importance when Hartwell and Pember (17) obtained evidence that the injurious effects of acid soils on certain plants was due to aluminum rather than to hydrogen ions. Subsequent work, however, has indicated that the matter is far from simple.

Except in the presence of sulfuric acid, it is probable that hydrosols of hydrated alumina are of general occurrence. Joffe and McLean (24) find that this colloidal aluminum may be in excess of the aluminum in the solution. The origin of aluminum appearing in solution in the aqueous phase of acidified soils is no doubt in part from solution of hydrated oxide, but there is evidence that so-called hydrogen-saturated clays are partly saturated with aluminum ions derived from lattice positions (2, 15).

Mattson (35) points out that when soils are electrodialyzed, a considerable amount of silica appears at the cathode. This must be transported as complex aluminosilicate cations. Mattson believes that $Al^{+++}$ ions appear only at very low pH values, and that normally aluminosilicate and aluminohydroxyl ions, $Al(OH)^{++}$, are the chief ionic forms of aluminum in the soil solution. More recently Gapon and Voshchinskaya (11, 12) have concluded that in a certain podzol soil which they studied, 90 per cent of the soluble aluminum was present as oxyaluminum ions, $Al_2O_3H^+$. Treatment of a KCl extract of such a soil with ammonium sulfate produces a precipitate of aluminum oxysulfate, $(Al_2O_3H)_2SO_4$. The remaining 10 per cent of the soluble aluminum is referred to colloidal alumina and $Al^{+++}$. The possible existence of complex ions of aluminum and organic acids has been mentioned. It is clear that even the soluble aluminum of soils can take very many forms and that our knowledge of the equilibriums involved is quite inadequate. The matter is, however, of great biological importance, as is easily appreciated when the great toxicity of the element in

aqueous culture solutions is compared with the reduced toxicity of the element in soil cultures, as judged from the aluminum concentration in displaced soil solutions. Gapon and Voshchinskaya (11) at least concluded that aluminum as $Al_2O_3H^+$ was far less toxic than as $Al^{+++}$, as indeed might be expected. It must also be remembered that aluminum is mobile in alkaline soils, and that since aluminum phosphate can be a source of phosphorus around neutrality, some aluminum can doubtless enter some plants at any pH.

## ALUMINUM IN VASCULAR PLANTS

### Mean content

With sufficiently refined methods, aluminum can apparently always be detected in the tissues of flowering plants. The most reliable data for herbaceous vegetation (47, 30, 58) indicate a mean content of about 0.02 per cent Al in the dry matter. Robinson et al. (47) found a like content in woody parts, but the spectrographic studies of de Rubies and Lemmel (48) perhaps indicate that such an estimate for wood is too high. On the basis of all these data, a mean value of 0.002 per cent Al in the living plant seems reasonable.

### Accumulator species

Certain species habitually accumulate amounts of aluminum vastly in excess of this small though variable amount of the element normally present [see Hutchinson (22) for full discussion]. The most remarkable cases are found in the Proteaceous tree, *Orites excelsa* R. Br., in which a deposit of a basic aluminum succinate, $Al_2(C_4H_4O_4)_3Al_2O_5$, in a cavity in the trunk is recorded (59); in various Theaceae (10, 68); in most Melastomaceae (10, 16, 23); in the Euphorbiaceous genera, *Baccaurea* and *Aporosa* (16, 23); in hickory, *Hicoria ovata* (46); in the whole family Diapensiaceae (23, 68); and in *Symplocos* (8, 10, 23, 26, 44, 46, 49, 68). Many of these cases have been discovered through the use of the plant as a source of mordant in the traditional technology of dyeing. In some species of *Symplocos*, cell inclusions occur which were supposed by Radlkofer to contain aluminum; Kratzmann, however, finds that after ashing, they are insoluble in HCl though soluble in HF. It is just possible that these inclusions contain an aluminosilicate of biological origin; in view of the demonstration by Vinogradov and Boichenko that nacrite can be hydrolyzed biologically, any case of possible aluminosilicate synthesis in an organism acquires great potential interest.

## DISTRIBUTION OF ALUMINUM IN PLANT BODY

A number of authors have concluded that there is a gradient in aluminum content, the amount falling off from the root to the leaf. This is certainly true in a number of species growing on very acid soil, the most extreme cases being the solfatara plants described by von Faber (10), in which accumulation occurs in the root, but not necessarily in the aerial parts. In more normal plants the leaf content of aluminum, as of other ash constituents, is often greater than that of the stem (28, 58).

## ALUMINUM IN PTERIDOPHYTES

Though the recent work of Tauböck, discussed hereinafter, apparently indicates aluminum to be an essential element in the nutrition of Pteridophytes, the few reliable analyses of ferns indicate that most species have no greater content of the element than do normal flowering plants (5, 30). There are, however, a number of microchemical qualitative determinations by Kratzmann (26) which suggest that when an adequate number of ferns has been analyzed the amounts of aluminum present will prove in general greater than in the spermatophytes. Two groups of Filicales appear to be undoubted accumulators. The Australian ferns, *Platycerium grande* and *P. alcicorne*, which are usually epiphytes, contain 3.9 to 5.5 per cent Al in the ash or 0.18 to 0.38 per cent Al in the dry plant (7). A number of species of tree ferns of the family Cyatheaceae are aluminum plants (5, 68); good analytical data, on taxonomically determined specimens, are restricted to Tauböck's record of 6.2 per cent Al in the ash of *Alsophila australis*, though in culture the supply could be reduced to an undetectible amount without injury to the plant.

The few species of Equisitales that have been adequately studied, and *Selaginella* and *Psilotum* among the Lycopodiales, contain little aluminum, but in *Lycopodium* itself very marked accumulation has been known for over a century; the available information has been summarized by Hutchinson and Wollack (23). Some degree of taxonomy on the basis of ash composition is obviously possible in *Lycopodium* and the interest of the case is greatly increased by the fact that Manske and his associates (34) are building up a far more refined and quite independent chemical taxonomy based on the alkaloids found in these plants. A particularly interesting feature of the aluminum accumulation by *Lycopodium* is its specificity. Hutchinson and Wollack found no excessive accumulation of either iron or gallium in *L flabelliforme*, and also believed, though on not quite adequate analytical evidence, that the rare earth content of the plant is very low. This suspicion has been confirmed by Robinson, as is indicated in his contribution to the present series of papers. In this specificity the accumulating mechanism appears to differ from that in the hickory and probably that in *Symplocos* also. The low iron content is in marked contrast to cases where pathological accumulation of both iron and aluminum in diseased corn stalks has been described (18, 19).

## METABOLIC SIGNIFICANCE OF ALUMINUM IN PLANTS

The most interesting of the older experiments apparently indicating a metabolic role for the element is that of Sommer (60), who found pronounced stimulation, particularly indicated in the seed yield, on addition of 1 mgm. Al per liter to solution cultures supposedly free from the element. These experiments and some similar but much less striking observations of Lipman (32) on maize, should be repeated, with Steinberg's criticism in mind that the observed effects may be due to the accidental correction of a gallium deficiency.[2]

[2] Gallium-free $AlCl_3$ solution is easily prepared by extraction of the gallium with ether from a solution in 6 $N$ HCl.

Tauböck (63) grew 124 species of flowering plants in solution culture. Spectrographic control of his medium indicated that it contained less than 25 $\gamma$ Al per liter. He observed no symptoms of aluminum deficiency, and in eight species a second generation was successfully reared from seed set by the first. It must, however, be pointed out that the quantities of minor elements (boron, manganese, copper, zinc) added in Tauböck's experiments were of the same order of magnitude as the upper limit of Al concentration possible. Moreover, it was not practicable to avoid uptake of Al from dust through the epidermis of the aerial parts of the plant.

Although these and other experiments leave the metabolic role of aluminum in seed plants of normal composition somewhat uncertain, a few observations have been published suggesting that the element is of importance to accumulator species.

*Symplocos japonica*, according to Neger (41), grows much better in Knopf's solution containing 1.0 mgm.-atom Al per liter than in solutions containing 0.0, 0.1, or 10.0 mgm.-atoms. From all solutions, including the control, the plants acquired some microchemically detectable aluminum, but the uptake was greatest from the optimal concentration. No indication of control of acidity is, however, given in the description of the experiments.

*Vaccinium varingiifolium, V. lucidum, Rhododendron retusum*, and *Ficus diversifolia*, growing in certain excessively acid solfatara soils in Java, were found by von Faber (10) to require aluminum for normal growth, though in these plants accumulation of the element is confined to the roots. At least in the case of *F. diversifolia*, the control culture was acidified, and therefore one criticism that might be brought against Neger's experiment on *Symplocos* is excluded. Comparable experiments were performed by Yoshii (69) with like results.

Turning to the Pteridophytes, we find according to Tauböck a very different situation, for here both the accumulator species, *Alsophila australis* and two species of more normal composition, namely, *Aspidium Filix-mas* and *Polypodium proliferum*, all failed to develop normally unless 0.16 mgm. Al per liter was added to the buffered culture solution. Tauböck's observations on these ferns are in line with the results of Kratzmann (27) who, in somewhat ill-controlled experiments, found that spores of *Equisetum arvense* failed to produce normal gametophytes unless aluminum nitrate were present in the medium. A particularly interesting aspect of Tauböck's experiment is that although *Alsophila* required aluminum for normal development, the quantity needed is much less than that required to produce the aluminum accumulation apparently normal to the plant when growing in soil. The parent tree-fern from which Tauböck obtained his spores contained 6.2 per cent Al in the leaf ash, whereas his plants, though permitted to grow in culture in the presence of 0.16 mgm. Al per liter, failed to accumulate the element. It would appear that a mechanism has been developed to permit the entry of the element, but not to regulate the excess consumption of the large quantities normally present in the environment. This, however, can hardly be true of the other ferns that he studied, for in *Aspidium Filix-mas*, Church (5) found only traces of aluminum, though Stoklasa (62) notes, probably

quite unreliably, 0.51 per cent Al in the ash of the aerial parts. Conceivably such species may have developed a more accurate regulatory mechanism, though, as has been noted, it is possible that the aluminum content of ferns is somewhat higher than of flowering plants. It is, moreover, doubtful whether mere excess consumption will explain the taxonomic regularity of accumulation in *Lycopodium*, where it is reasonably certain that the high capacity to accumulate the element, often in rather constant amounts, represents an evolutionary specialization.

All these experiments can be criticized on the grounds that gallium may be involved as an impurity in the aluminum salts used, and all should be repeated with such a thought in mind. In the case of *Symplocos*, experiments should also be conducted with the rare earth elements. Tauböck's work at least indicates unequivocally that the three ferns studied require aluminum, or some element associated with aluminum, in much greater quantity than do most of the flowering plants. To the present writer, who is possibly overimpressed by the specificity of the aluminum-accumulating mechanism in *Lycopodium*, the most reasonable explanation of the observations is that aluminum is actually required by the ferns and probably by the other vascular cryptogams.

Apart from these experiments mention may be made of work by Sergeiev and Sergeieva (56, 57), which appears to indicate an increase in the frost resistance of wheat, due to aluminum, and of the remarkable observations of Liebig, Vanselow and Chapman (31), demonstrating that aluminum protects citrus cuttings from the poisonous effects of a slight excess of copper. The presence of aluminum had no effect on the distribution of copper in the plant, nor was any evidence of precipitation of copper by the aluminum in the culture medium to be noted. The well-known effect of aluminum in the production of blue flowers in *Hydrangea* has been the subject of many investigations, admirably reviewed by Chenery (4), who showed that the blue color is due to formation of an aluminum complex of a delphinidine diglycoside.

### EXCESS ALUMINUM AS AN ECOLOGICAL FACTOR

By far the most important aspect of aluminum is its action, when present in excess in soluble form, as a limiting factor to the growth of certain plants. This aspect of the biogeochemistry of the element was first clearly indicated by Ruprecht (50), Ruprecht and Morse (51, 52), and Hartwell and Pember (17). An immense amount of work has been done on the problem, and it would now appear that acid soils are unsuitable for some plants on account of their acidity, but that, in other cases, the increasing concentration of hydrolyzate-oxidate elements limits the growth of plants. In view of the number of contributions that have appeared on this matter, a synoptic summary of results alone can be attempted in the present review. A full summary of the literature has been given in an earlier review (22).

In a number of cases amounts of aluminum, as $Al^{+++}$, of the order of 1 mgm. per liter can exercise a distinctly unfavorable effect in solution cultures.

There is much interspecific variation in the threshold or fatal doses of aluminum; Gilbert

and Pember (13) have adduced evidence that such variation in tolerance may regulate competition between certain grasses and dicotyledons.

There is a great discrepancy between the threshold toxicity of $Al^{+++}$ in solution cultures and the amount present in soil solutions in pot cultures of plants just showing injury. Thus Sommer (60) found 2 mgm. Al per liter injurious to wheat in solution culture, whereas Mattson and Hester (36) did not get an effect with two electrodialyzed soils adjusted to various pH values until 1 or 2 mgm. soluble $(Al, Fe)_2O_3$ per 100 gm. soil were present, corresponding to at least 5 to 10 mgm. Al per liter of soil solution and probably considerably more. Mattson and Hester also found that silication of a soil not merely reduced the pH at which a given amount of aluminum appeared in solution but also increased the tolerance to such a given concentration. The form in which aluminum is present in the soil solution is clearly of great importance. Mattson and Hester have given evidence that aluminosilicate ions exist and believe them less toxic than $Al^{+++}$. Gapon and Voshchinskaya (11, 12), as has already been indicated, found evidence of $Al_2O_3H^+$ ions, which they concluded are relatively nontoxic.

Phosphate treatment and liming both reduce the aluminum toxicity of a soil. In the case of lime treatment, presumably a rise in pH causes less aluminum to go into solution. In the case of phosphate treatment the mode of action is obscure. Burgess and Pember (3) and Pierre and Stuart (42) found that addition of phosphate did not cause any decrease in the aluminum uptake but did cause a marked increase in phosphate uptake. It is possible that the aluminum is fixed as the relatively insoluble $AlPO_4$ within the plant, particularly in the roots. Some workers, notably Sergeiev and Sergeieva (56, 57), believe that there is a specific ionic antagonism between $Al^{+++}$ and $PO_4^{---}$, but the evidence cannot be regarded as satisfactory. The experiments of Trenel and Alten (64) are of considerable interest. In one series, corn plants with divided roots were exposed on one side to a complete nutrient solution without aluminum, and on the other, to aluminum solution. Injury was limited to the roots exposed to aluminum. In another series, aluminum was added to a phosphate-free nutrient solution on one side, and phosphate supplied on the other. Here the whole plant was inhibited. The percentage of N, K, Ca, and P in the dry matter of such plants was, however, greater than in the controls, so that these elements were taken up by the injured roots in excess of the amount the depauperated plant could effectively utilize. In most cases, however, the relative magnesium content was reduced, but one series failed to show this effect. It is tempting to suppose that the root injury may limit uptake and utilization of magnesium and therefore assimilatory processes, but the exceptional case probably excludes such an interpretation. Interference with normal copper metabolism may conceivably have to be considered in view of the results of Liebeg, Vanselow, and Chapman (31).

## ALUMINUM IN ANIMALS

Most of the aluminum taken up by herbivorous animals is apparently excreted with the feces; at least a part of this has apparently been absorbed and passed into the bile. The net result of the assimilatory process is, however, to produce an organism considerably poorer in aluminum than is the food. The best results (9, 29, 37, 38, 39) indicate that whereas mammalian muscle is very low in the element, the viscera may contain a little over 1 mgm. Al per kilogram wet. Myers and Mull (40) and Kehoe, Cholak, and Story (25) find like amounts in man; Lundegårdh and Bergstrand (33), investigating many human livers, however, found a mean value twenty or thirty times greater than that of other investigators on man or other mammals. The explanation of this discrepancy is not clear, as Lundegårdh and Bergstrand's results for other elements agree with those of previous investigators. For the present the best general value for

mammalian tissue is probably about 0.5 mgm. per kilogram, representing about one fortieth of the quantity of the element in the food. Scoular (55) found no evidence of retention of aluminum in the growing human child, though she (53, 54) was able to detect retention of zinc and copper. Despite the low quantity of aluminum present in mammalian tissue and the negative results of all modern experiments producing aluminum-deficiency symptoms in mammals, there is evidence from the work of Horecker, Stotz, and Hogness (20) and of Potter and Schneider (43) that aluminum is involved in the succinic dehydrogenase-cytochrome C system, which is the chief mechanism for oxidation of succinate in the mammalian body. It is supposed that aluminum is involved in the reaction between cytochrome-C and its reductant, presumably succinic dehydrogenase. Some other tervalent elements, namely, Cr, Nd, La, and Sm, can substitute for aluminum. Analytical evidence, both from the enzyme preparations themselves and from the known composition of the mammalian body, strongly indicates that aluminum is actually the element involved *in vivo*. It is noteworthy that on the diet containing the least amount of aluminum yet available, which supplied 1 to 1.5 $\gamma$ daily to the rats used in the experiment, the liver accumulated 90 to 107 $\gamma$ per kilogram of the element, and that increasing the aluminum in the diet twentyfold to thirtyfold caused but a threefold increase in the liver aluminum (21).

Finally it is desirable to point out briefly that although massive doses of aluminum in stoichiometric excess of the phosphate intake may cause a rachitic condition, there is little evidence that this would ever happen from ingestion of human food prepared from aluminum-containing baking powders. The supposed injurious effect of aluminum cooking vessels appears to be quite apocryphal. The most striking species of accumulator plants, however, certainly contain a great excess of aluminum over phosphate, and would constitute by themselves impossible diets for herbivorous vertebrates unless, as is very unlikely, the aluminum is in some form incapable of reacting with phosphate prior to absorption of the latter in the intestine.

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# BORON IN PLANT LIFE—A BRIEF HISTORICAL SURVEY[1]

## JOHN W. SHIVE
### *New Jersey Agricultural Experiment Station*

The importance of the inorganic elements involved in the development of a plant, other than those usually considered nutritive, was greatly underestimated or was given no consideration at all in agricultural practices up to within a decade or two ago. But the roles which these elements play in the metabolic processes of plants, whatever these roles may be, have been found to be of such fundamental significance that today the so-called trace elements are receiving a major share of attention both from the soil scientists and from the plant physiologists. This is particularly true of the element boron and the role which it plays in the economy of the plant and around which a vast literature has been assembled during the past quarter of a century.

The great bulk of this investigational literature is descriptive in nature, portraying and illustrating symptoms of diseases which develop when boron is deficient in the environment of the plant, or it is descriptive of the injury to plant structures which results when the element is present in quantities in excess of that required for growth and development. Though the investigations dealing with the observational or qualitative phases of the boron problem are exceedingly important and must precede the more quantitative studies, so much of this foundation in natural fact has already been accomplished that further experimental studies along these descriptive lines must now be subordinated to the more fundamental quantitative type of research. The disease symptoms of shoots and roots of virtually all the important agricultural species, which occur as the result of boron deficiency and of boron excess in the growth medium, have been so thoroughly described and so widely reported that they should provide adequate diagnostic guides both for field observation and for the more basic researches carried out under controlled conditions. A volume (18) of considerable size has recently been published which constitutes a most valuable contribution to our knowledge of the symptoms of nutritional disorders related to deficiency or excess of the inorganic elements essential to plants. In this publication boron is given a prominent position. The purpose of the volume is stated by its editor as follows: "The purpose of this book is to help us to recognize the signs of nutritional deficiencies in crop plants. It was written by scientists who have made a close study of this subject, each in his own particular field, for many years." The hope may be expressed that, though this is the first book of its kind, it may not be the last.

## DISCOVERY AND DISTRIBUTION OF BORON IN PLANTS AND SOILS

That boron occurs naturally in plants was first discovered nearly a century ago by Wittstein and Apoiger (46), who found boric acid in the seed of *Maesa*

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*picta.* The significance of this discovery was not apparent until years later when Baumert (5) in 1888 detected boron in wines, and Crampton (16) in 1889 and Callison (14) in 1890 found boron in various fruits and predicted that the occurrence of boron in the plant kingdom would prove to be much more general than their experiments indicated or than had previously been supposed. This prediction received emphasis and support when Hotter (19, 20) in 1890, and again in 1895, found boron not only in the fruits of many species but also in the leaves and tissues of a great variety of plants. Finally in 1895 Jay (22) suggested, after exhaustive analyses of many plants and plant products, that boron might be universally distributed throughout the plant kingdom. It is now generally accepted that this element occurs universally in the autotrophic plants and it is known to be distributed in at least some of the heterophytes such as the mushrooms. It was concluded, as the result of many researches at this time, not only that boron is widely distributed in the plant kingdom, but also, since the soil is the source of boron in the plants, that it occurs generally in soils, but only in very minute quantities in some. Small amounts of boron were detected in plants grown on soils which were so deficient in this element that it could not be identified by the most delicate chemical test. Furthermore, it was discovered that plants differ widely in their ability to absorb boron from soils and water. Even at this early date it was recognized that the agricultural monocotyledonous plants (wheat, rye, oats, barley, corn, etc.) have a much lower capacity for absorbing boron than have the dicotyledonous plants.

One of the most comprehensive surveys of the distribution of boron in the soils of America was made recently by Whetstone, Robinson, and Byers (44). This work, however, represents much more than a mere survey of boron distribution. It deals authoritatively with such matters as the content and form of boron in many soil types and the relation of boron content to soil parent material and great soil groups. It differentiates between the soluble and insoluble boron fractions and relates these to soil properties. It points out three large regions in the United States in which soils are likely to be deficient in boron for plant needs and why. The three regions are the Atlantic Coastal Plain extending westward to the Appalachian Mountains; a region across northern Michigan, Wisconsin, and Minnesota; and the Pacific coastal region and the Pacific Northwest. These regions agree, in the main, with those indicated in a previous report by Purvis (33), which includes an outline map of the United States on which are marked areas where soils are known to be boron deficient from the standpoint of plant requirements. The authors assert that natural boron toxicity is unlikely except in arid regions where soluble boron salts may accumulate in the soil. Soils which were formed under normal rainfall were found to contain from 4 to 88 p.p.m. total boron, and the range of available soluble boron extended from 0.4 to 64.8 p.p.m. and averaged 17.1 p.p.m., which represents 50 per cent of the total. Boron was detected in all of about 300 soil samples.

A recent survey, local in its interest but an outstanding and most important work of this nature, is that dealing with the boron needs of the soils of New Jersey, reported by Reeve, Prince, and Bear (35). In this survey use was made

of laboratory, greenhouse, and field tests of both plants and soils. Based on such tests, crop responses were studied on 350 widely distributed farms on which test plots were established. This is the most comprehensive work of its kind yet carried out and provides an excellent guide for agricultural practices from the standpoint of boron nutrition of plants in crop production.

## BORON AS A TOXIC AND AS A STIMULATING AGENT

For more than a quarter of a century following Jay's work in 1895, investigations of the boron problem were concerned in general with the toxic action of boron compounds on plants and in particular with their stimulating effects, primarily for economic reasons. During this period the essential nature of boron for growth and development had not yet become a subject of serious consideration, although Agulhon (1, 2, 3) in 1910 suggested that the element, occurring only in very minute amounts and exercising a function which he regarded as catalytic, might be an essential factor in the life of certain groups of plants subjected to particular conditions. The work of Agulhon and of Bertrand (8, 9), more than that of any other investigators up to 1912, had fixed attention on the probable significance of boron and its practical importance in agriculture. Their studies of the growth-promoting and stimulating effects of this element at low concentrations and its growth-retarding and toxic properties when present in quantities which exceeded those in the range of stimulating concentrations were exhaustive.

While Agulhon's work set the pattern of boron research during the early years of the present century, Brenchley's outstanding investigations in England, beginning in 1914 (11), were of even greater significance and definitely paved the way for establishing proof, a few years later, of the essential nature of boron in plant life. Brenchley's work was characterized by great care in experimental procedure and by a high quality of refinement in both method and material at all stages of her experimentation. She attempted to establish approximately the lower limits of toxic concentrations of boric acid for several species as well as the upper limits of stimulating concentrations. Thus, for example, she asserts that barley was injured by boric acid at concentrations of about 1:250,000 in water culture. At lower concentrations the response was indifferent. There were indications, however, that concentrations lower than 1:10,000,000 were stimulating, but that this must still be regarded an open question. Peas, on the other hand, were much less sensitive, the limit of toxic concentrations being about 1:50,000. Stimulation began at about 1:100,000, but was not progressive with concentration, since 1:100,000 boric acid in water culture was just as effective as 1:20,000,000, a flat curve connecting the two concentrations. Brenchley makes it clear, however, that limits of toxic or stimulating concentrations are meaningless unless they are definitely associated with and defined for certain important external factors which influence growth, such as season of the year, photoperiod, and particularly the nature of the substrates—solution, sand, and soil cultures—in which the plants are grown. She points out that

contradiction of results by various workers is frequently due to the fact that experimental methods are not given adequate consideration.

Investigations dealing with boron toxicity came into prominence in America during the first World War, when injury to crops in several states was traced to the use of potassium fertilizers which contained excessive amounts of borax. Conner (15) reported that enormous damage to crops was caused by the use of these fertilizers obtained from several sources. His experiments showed that the probability of injury to plants through the poisonous effects of boron in fertilizers is determined by many factors such as the nutritional status of the plants, method of application, seasonal conditions, crop grown, type of soil, and other factors. Similar results were obtained by Blair and Brown (10), Neller and Morse (31), and many others. It was demonstrated clearly by the large scale experiments of these investigators not only that the poisonous effects of borax in fertilizers are strongly modified by local conditions, but also that the relation of boron to plant life in general is a matter of great complexity.

Although this early American work contributed little of a fundamental nature, it stimulated a strong interest in the investigation of the urgent problems related to plant nutrition in general and brought to the fore the great importance of more intensive researches directly concerned with problems of the so-called minor elements, particularly boron, in the growth and development of plants both from the point of view of fundamental research and from the standpoint of agricultural pursuits.

### INDISPENSABILITY OF BORON FOR PLANTS

Since the beginning of the present century sporadic attempts have been made to establish proof of the indispensable nature of those elements which had been found to be distributed in plants and soils almost universally in minute quantities only, but which were not included in the category of those elements which had long been considered essential to plants. Boron occupied a prominent place on this list of "minor elements." Evidence accumulated during the first decade and a half of the century led to the general view that inorganic elements, such as boron, required by plants only in trace quantities, are to be regarded, perhaps, not as indispensable but only as stimulating. This general attitude, although erroneous, was nevertheless a natural outgrowth of the times and perhaps to be expected at that stage of the progress made in plant nutrition, since the usual experimental technique which had long been employed was too crude and the materials used were too unrefined to disclose the essential nature of specific elements required by plants in minute traces only. The value of such an attitude to the evolution of the boron problem, however, should not be underestimated in view of the fact that, even at the present time, it is not always a simple matter to differentiate with positive assurity between that which merely stimulates and that which is indispensable for growth and development, particularly since the degree of purity and the state of refinement of materials and methods are determinative factors in any attempt to establish proof of the indispensable nature of an element, as was so forcibly demonstrated (37) during the later development of this most important problem.

Experimental evidence, already considered, of the stimulating effects and of the toxicity occasioned by the use of minute amounts of boron, both in artificial culture and under natural conditions, provided the incentive for intensive quantitative studies. These gave impetus to the development of more highly refined methods of procedure than had been employed previously, and compelled a higher degree of purification of materials than had yet been attained.

The first investigator to take such a comprehensive view of the problem was Mazé (28, 29, 30). By the use of new and greatly improved methods of experimentation he produced evidence so convincing as to lead him to the conclusion that not only boron but also other elements not previously considered essential might be found indispensable for green plants. The correctness of this point of view is no longer in doubt, despite the fact that Mazé's conclusion was based on results obtained with only one species, maize. Mazé's work did not receive the immediate recognition which it deserved and has apparently been overlooked or has been disregarded by many subsequent investigators, but his general conclusions with respect to boron received strong support from the extensive and very thorough work of Warrington (42) with the broad bean and later from the work of Brenchley and Warrington (13).

Warrington (42) in 1923 was among the first, probably the first, to furnish incontrovertible evidence that boron is indispensable for plant life, but this evidence refers to a single species only, the broad bean. The evidence is provided by the fact that the broad bean did not complete its cycle but died in a characteristic manner in the absence of boron. Preliminary results with other species, such as barley, crimson clover, and several species of beans, led to the general belief that boron is essential for these species also, but the evidence was held to be inconclusive. Several years later, however, Brenchley and Warrington (13) produced unmistakable evidence that these species also, as well as several others, required boron to complete their growth cycles. Nevertheless, they drew a sharp distinction between plants for which boron is essential and those for which it is beneficial only, but they did not preclude the possibility that the difference between the two classes might prove to be merely a matter of degree in boron requirement. These authors conclude also that the form in which boron is presented is immaterial and that its function is unaffected by the nature of the growth substrate and appears to be nutritive rather than catalytic, since a continuous supply is required throughout the life of the plant.

The work which deals with the question of the indispensability of boron in the most comprehensive and authoritative manner was reported in a series of publications by Sommer and Lipman (37) and by Sommer (38). Their work makes it clear that only through exercise of the greatest precautions can the problem of essential minor elements, including boron, be solved. The authors insist most emphatically that there is no solution culture technique so exacting as that which is designed to prove the indispensability of an element for the life and growth of the green plant and that the ordinary solution culture technique is wholly inadequate for the solution of the subtler phases of the general problem. For this reason they describe in great detail their entire procedure including methods of refinement and purification. By means of this highly refined tech-

nique Sommer (38) has been able to establish the indispensibility of boron for a large number of species of both monocotyledonous and dicotyledonous plants including corn, sunflower, peas, vetch, barley, buckwheat, dalhia, potato, lettuce, millet, sugar beet, castor bean, sorghum, kaffir, pumpkin, mustard, and flax. Sommer and Lipman (37) were the first to provide evidence so clear and of such a decisive nature as to justify their conclusion that the need of boron appears to be general for the higher green plants and that this may be stated as an empirical law.

<center>NATURE OF BORON-DEFICIENCY EFFECTS</center>

The distinctive characteristics of external visible symptoms of boron deficiency have been more or less completely described by most of the investigators whose work has dealt with some phase of the boron problem as it relates to the growth and development of plants. Representative among these investigations is the work of McMurtrey (26), whose descriptions and illustrations in a series of papers on boron deficiency effects in tobacco are outstanding. Though the symptoms are always associated with metabolically active tissues and are distinctive for each species, they differ widely from species to species, as a result of structural differences and relative positions of the active tissues which are affected. These different manifestations of boron deficiency in different species have been given disease names, but it is only comparatively recently that many of them have been traced to boron deficiency as the causal agent. Some of these deficiency diseases were named and described long before their causes were understood. A single example will provide sufficient illustration. In 1924 Foster and Weber (17) described a non-parasitic disease of celery which they named "cracked stem," and ascribed as its probable cause a combination of climatic factors, use of an unbalanced fertilizer, and excessive use of lime. It was not until 1937 that Purvis and Ruprecht (32) traced the cause of the disease to a deficiency of boron. In some cases a great many years elapsed between the discovery of the disease and the final discovery that it is caused by boron deficiency. This is what Atwater (4) refers to as "the ancient history of boron deficiency symptoms." A considerable number of these so-called nonparasitic diseases associated with boron deficiency have been reported and described. Among them may be enumerated: top sickness of tobacco, heart rot of beet, cork disease of apple, brown rot of cauliflower, cracked stem of celery, Raan of swedes, and many others. Some have been described many times, and the boron literature teems with these descriptions and with researches dealing with the applied phases of this boron problem, since these phases are of greatest immediate importance from the economic point of view.

Researches dealing with the more fundamental aspects of the problem of boron-deficiency effects, however, are not entirely lacking. These are usually intensive morphological and histological studies of tissue abnormalities induced by deficiency of the element in question. The first important study of this nature was undertaken by Warrington (43), who was the first to point out the now well-known internal features of tissue abnormalities which result in the absence of

boron. The more important of these are death of the apical meristem, failure of young roots to emerge or complete their development, irregular cell division accompanied by discoloration of cell walls, hypertrophy of cambial cells followed by degeneration and discoloration, disintegration and discoloration of phloem and ground parenchyma, poor development and ultimate breakdown of xylem tissue, which results in blocking the conducting systems. In a similar manner Sommer and Sorokin (39) made a detailed study of the structural changes in the cells and tissues of the root tips of *Pisum sativum* induced by the absence of boron from the culture solution.

The outstanding and most significant work dealing with the "histologic-pathologic effects of boron deficiency" was reported in a series of publications by Walker and his associates between 1941 and 1943. This work is admirably summarized in a symposium paper by Walker (41), who has shown that the first symptoms of boron deficiency are not externally visible, since pronounced necrosis is not the first reaction to boron starvation. One of the first effects is increase in cell numbers and size and decrease of differentiation in the meristematic regions. Abnormal development of conductive tissue leads indirectly to the characteristic externally visible symptoms, such as tissue distortions, abnormal anthocyanin development, the usual stunting of growth, and reduced or complete suppression of yields. Pathological symptoms in the form of necrosis are only the end results of a series of histologic changes induced by abnormal cell physiology and differentiation. The work of this author and his associates will provide an excellent approach to the problem of how boron functions in the mechanisms of tissue building and in the metabolism of plants in general.

### RELATION OF BORON TO OTHER ELEMENTS IN NUTRITION OF PLANTS

During the last decade, boron research as it relates to plants has taken a sharp trend away from the highly practical, qualitative, descriptive phase toward the fundamental, more quantitative type of investigation. This trend undoubtedly grew out of the necessity for more fundamental knowledge to provide a better understanding of the chemical and physiological relationships which boron may enter into with the nutrient elements essential for plants, since such knowledge is directly applicable to and is intimately concerned with certain economic problems relating to fertilizer chemistry and to fertilizer practices in agricultural pursuits. In fact, suggestions have been made from time to time over a period of years that boron functions in plants in conjunction with other ions, particularly with the metallic cations calcium and potassium. Recently the nitrate and phosphate ions also have been included in this category (6). The existence of such relationships in plants has been well established. That they represent one of the most important phases of the boron problem, both from the scientific and from the economic point of view, is no longer in doubt. As has been well stated by one author (6), however, the functional roles of boron have not yet been well integrated despite the mass of investigational literature on this element in nutrition. On the other hand, it may be said that there is as yet no experimental evidence which provides even a good clue to the mechanisms involved in

the functional relationships between boron and other nutrient elements in cell metabolism.

Brenchley and Warrington (13) were among the first to suggest that a functional relationship exists between boron and calcium in the plant. They pointed out that even with an adequate supply of calcium at the roots, this element cannot be effectively utilized in the absence of boron, and that in some way boron enables the plant to absorb more calcium in a given time or to utilize it more efficiently in metabolism after it is absorbed. This is in line with later work by Marsh and Shive (27) who found that the metabolically effective calcium which is maintained in the soluble available state in the active plant tissues is directly correlated with the supply of available boron in the same tissues.

Several investigators have provided experimental evidence which shows that the symptoms of boron deficiency and toxicity are tremendously influenced by quantitative relationships in the plant between boron and the metallic cations, particularly calcium and potassium. Thus Jones and Scarseth (24) have shown that a plant will make normal growth only when a certain balance in the intake of calcium and boron exists. If this balance is upset by a too small intake of calcium the plant will have a very low tolerance for boron. If, on the other hand, the balance is upset by an excessive intake of calcium the plant will have a very high boron requirement. Boron can be added in larger quantities to alkaline or limed soils than to acid soils without causing boron injury to plants. The authors assert that the importance of the proper balance of calcium and boron, both in quantity and proportion, can not be overemphasized. Factors which affect this balance must be taken into consideration in interpreting any condition in the dynamic-soil relationships, and they suggest that a quantity of such data would have valuable application in predicting the boron needs of the plant from the analysis of its tissues.

Results obtained by Reeve and Shive (34) show similar relationships between calcium and boron in the metabolism of the plant. Furthermore, they have produced sufficient evidence to suggest that the response of the plant toward boron is determined by the direct and intimate relation between calcium and boron in metabolism. They also report that potassium in the growth substrate has a very definite influence on the accumulation of boron in the plant tissues, the rate of boron absorption and accumulation increasing as the potassium concentrations in the growth medium are increased. This effect is particularly pronounced at high boron levels and may result in severe boron toxicity. Boron-deficiency symptoms also are strongly intensified with increasing concentrations of potassium. Field experiments by White-Stevens (45) and others have corroborated these findings. Potassium, however, appears to influence the response of the plant toward boron indirectly through its determinative effects upon the processes involved in the absorption and accumulation of calcium, a suggestion proposed also by Jones and Scarseth (24).

Relationships between boron and the nutrient anions in plants have not been so extensively investigated as the relationships between boron and the nutrient cations. Beginnings in this direction, however, have been made. But studies

involving the association of boron and the nutrient anions in metabolism invariably and unavoidably inject a consideration of the role of boron in protein synthesis and degradation (40) as well as sugar accumulation (21) and utilization in respiratory breakdown (23). These processes are so complex and involved that attempts at the interpretation of data relating to them, at best, are only suggestive and usually mere conjectures. Nevertheless, more and better knowledge of the role which boron plays in these complex processes is so important that even suggestions and conjectures must be explored and clarified by continued investigation along these lines. When the functional relationships between boron and the nutrient anions in metabolism are referred to the symptoms of favorable or unfavorable plant response, such as symptoms of deficiency and toxicity, the evidence is much more specific and conclusive. Thus, Beckenbach (6) found that plants grown with solutions containing an adequate nitrate supply required many times more boron than did nitrate-starved plants, and that plants grown with solutions deficient in phosphates require more boron than do plants receiving ample phosphates. This evidence is conclusive and has been substantiated by others. But when the author endeavors to interpret the evidence in support of the theories that boron is functional in protein metabolism probably through a direct effect on carbohydrate utilization, or that phosphate and borate ions may function interchangeably as essential juice buffers, the evidence is not too convincing but is, nevertheless, most useful and important in providing new leads for further investigation.

It must not be overlooked that in the substantial progress which has been made toward the elucidation of the important roles which boron plays in the nutrition of plants, some notable and virtually indispensable contributions have been made in devising and refining the analytical procedure of testing for boron. Outstanding among these is the procedure of Berger and Truog (7), which has been almost universally adopted for boron analyses of both plant and soil, and has become a standard method. This, together with the spectroscopic method proposed by McHargue (25) and his associates, has done much to facilitate the investigations of boron in plant and soil.

The indispensable role which boron plays in the life of the plant is not strange or remote in view of the peculiar properties of the element and the great versatility of its compounds, which have made it almost indispensable also in the arts and trades. Boron has contributed many items of value to civilization over a period of more than half a century. It is used in the preparation of raw silks for weaving and hides for tanning. It enters into the manufacture of the fine, stain-resisting glaze of the finest potteries and ceramics, and into the making of common and chemically resistant glass. In metallurgy, it plays a prominent part in the production of many alloys. It is used in the preparation of antiseptic solutions, medicated bandages, and cosmetics, and in the manufacture of rayon fabrics. Most glazed papers contain borax in their coatings. It has made nickel plating a practical commercial process and has aided immeasurably in the art and practice of brazing and welding. It is used extensively as a deliming agent in the manufacture of a number of important commercial products. It finds other

uses not here enumerated. It has been suggested (36) that the peculiar properties of boron which render it so versatile and make its compounds so useful in the arts and trades are also the ones which render it indispensable in the growth and development of the plant.

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# INFLUENCE OF CHLORINE ON PLANTS

## A. R. C. HAAS

*University of California, Citrus Experiment Station*

Chlorine occurs in most soils (71) and plants (49, pp. 352–356), and in the latter largely as water-soluble chlorides (39). Early experiments with buckwheat plants in Cl-free solutions resulted in abnormal plant growth.

## Cl REQUIREMENTS OF PLANTS

The influence of Cl upon plants (49) depends upon the nature of the plant, the growth medium, and the climatic conditions. The same growth was obtained with wheat in solution cultures properly balanced (49), regardless of the amount of Cl added.

The deficiency effects of Cl lack distinctiveness. No reference to them is found in a discussion (9) of trace elements. The conclusion has often been reached that for healthy growth and development buckwheat plants require no more Cl than the small amount contained in the seed (49). Although Cl has been considered by some (71) as essential for the growth of corn, others (19) have grown healthy plants without its presence in the nutrient solution. Some (71) would go so far as to regard Cl as beneficial to most crops. Beneficial effects of this element were reported [Eaton (17)] for the growth of tomatoes and cotton in sand and solution cultures. Lipman (43) found that buckwheat and peas were improved when Cl was present in the solution cultures. With buckwheat, both the total dry matter and seed production were increased, whereas in peas only the seed production was increased. Low concentrations of Cl were reported [Koenig (41)] as increasing the growth of plants. Alfalfa was affected beneficially [Lomanitz (49)] when varying amounts of NaCl were substituted for $KNO_3$ in culture solutions. The application of NaCl [Rudolfs (49)] to asparagus beds increased, at certain concentrations, the average number of stalks. Small amounts of NaCl also stimulated the growth of oak, birch, and maple trees (49).

## DETERMINATION OF Cl

Chlorine can be determined as silver chloride either by gravimetric or volumetric methods. Difficulties encountered with the *o*-tolidine method are reported as being overcome by the use of $H_3PO_4$ (29). In the colorimetric method *p*-aminodimethylamine is claimed to be of use (12). The alcoholic extraction and precipitation with silver nitrate is described as a rapid method for tomato products (7). The loss of Cl in the ashing of plant material is overcome by the use of excess $Na_2CO_3$ and limitation of the temperature of ashing to 600°C. (54). The removal of water-soluble salts by filtration after the initial ashing, followed by the reignition of the dried residues, facilitates the determination by the gravimetric method (28). The atomic weights of Cl obtained from the separation of isotopes in HCl (33) were 36.956 for the heaviest fraction and 34.979 for the lightest.

## Cl CONTENT

Rain may have a variable content of Cl. At Bombay (51) during the monsoon, the rain contained 2.7 to 26.5 p.p.m. The osmotic values in plants of saline areas in Bengal, India, varied from 11 to 44 atmospheres in various species, and the Cl accounted for 4 to 80 per cent (usually over 50 per cent) of the osmotic pressure (38). Some plants contain only traces: the Cl in all the corn plants on an acre producing at the rate of 100 bushels per acre may be equivalent to that in the rainfall (59). Cotton plants collected from 28 different soil series exclusively used for cotton production in South Carolina contained 0.679 per cent Cl in the plant and 8.301 per cent in the ash (14). An average of 0.38 per cent was contained in 34 samples of African tobacco, much lower than in American tobacco. The too rapid burning of the African tobacco was corrected by adding 50 pounds NaCl or KCl per acre with the usual fertilizer (1). The extremes of Cl content in Kentucky burley tobacco were: 0.02 to 1.05 per cent; in dark grades the extremes were: 0.04 to 2.99 per cent (61). The Cl content of tobacco leaves varied from 0.422 per cent for lower leaves to 1.011 per cent for upper leaves of the same plant (60). Nitrate had no influence on the Cl content (60).

Gradients occur in the Cl distribution in avocado fruits (27). The percentages in the dry matter of healthy avocado leaves in the orchard ranged from 0.09 to 0.33 per cent, whereas leaves affected with tipburn contained an average of 1 per cent (26).

The use of fertilizers containing Cl increases the Cl content of the sap of corn plants, and the increase is partly proportional to the amount supplied by the fertilizer (53). The content in potatoes also increased with the amount applied in potash fertilizers (55).

In solution cultures, additions of $SO_4$ or N to the medium decreased the Cl intake by potatoes and flax. Additions of Cl to the medium decreased the N in flax (5).

Roots of walnut and orange seedlings usually contained more Cl than the tops. Orange leaves contained 0.28 to 22 per cent Cl in their ash (49).

The average Cl content of cell sap of Nitella (36) was 0.128 $M$, much higher than that of the water in which the plant lived. The amounts present in tissue fluids (30) of the Egyptian type of cotton were higher (28 to 189 per cent) than in those of the Upland type. This may indicate a greater capacity of the Egyptian type for growth in saline soil. In the leaves of certain species of trees (66), Cl increases with leaf age, in others it decreases, and in still others there is no regularity. The deep roots of sugar cane are reported (18) to absorb Cl vigorously. Barley plants accumulated Cl more readily than $SO_4$ (20); $SO_4$ reduced the Cl accumulation, but the addition of Cl had no effect on $SO_4$ accumulation.

## Cl AS A FERTILIZER

Published results on the value of Cl as a fertilizer are confusing, probably as a result of poorly defined environmental conditions. Applications of 20 to 30

pounds of Cl per acre were reported [Garner *et al.* (49)] to have increased the production of tobacco and to have given the maximum stimulating effect.

Chlorination of soil was said to have increased crop yields (23). When fields of sugar cane were irrigated with brackish water, the cane juice was of low purity and of high and almost directly proportional K and Cl amounts (24). Certain soils richer in chlorides than others were claimed to produce better quality flax (10).

Chloride fertilizers frequently cause currant leaves to show edge blight resembling K deficiency (8), a condition that occurs when enough K is present for normal requirements but insufficient to combine with all of the Cl present in the leaves.

### TOLERANCE OF PLANTS TO Cl

Some crops are tolerant to high Cl, whereas others are more sensitive. The ratio of monovalent to divalent bases in the soil is considered of importance (48) in the tolerance of trees to Cl. Lemon trees (17) were found to be four or more times as tolerant to $SO_4$ as to Cl. Date palms are considered to be tolerant of large concentrations of Cl; however, in the Deglet Noor, one of the most important date varieties, the pinnae and fruit pulp rank very low in their accumulation of this element (28). Sugar beets and asparagus are considered as being very tolerant to Cl. On the other hand, clover and sugar cane are reported to be extremely sensitive to its presence (2). It was found (46), however, that sugar cane stalks can produce roots in a solution of chlorozene (4.6 grains in 10 liters). Cotton is reported (49) to be tolerant of Cl when KCl is the source of this element in the field. *Atriplex hastatum*, *Picridium vulgare*, and *Sonchus oleraceus* are said (52) to be resistant to 1.7 per cent Cl in soil, black cabbage to 1.2 per cent, and Salsola soda to 4.1 per cent. The stage of development of maize seedlings is important in determining the amount of NaCl they can withstand in solution cultures (49).

### TOXICITY OF Cl

Whereas small concentrations of Cl may be beneficial to some plants, excessive amounts usually are highly toxic. The age of the plant (49) is an important factor in the degree of toxicity of NaCl. When the entire source of K and N is from KCl and $NH_4Cl$, the amount of Cl from such a mixture, at the rate of 900 pounds per acre, is excessive for the best growth and yield of cotton (62). The use of $NH_4Cl$, though rational for neutral soils, is not suitable in acid soils because of the high Cl content (63).

The addition of KCl to the soil in orange groves at the rate of 30 to 160 kgm. per hectare was accompanied by injury to the leaves of young shoots, especially at the higher rates of application. The use of $K_2SO_4$ in equal concentrations was not injurious (37). For citrus trees the irrigation water should not contain more than 150 to 200 p.p.m. of Cl (40). Damage to citrus trees (57) occurred when the irrigation water contained 350 p.p.m., and death occurred at much higher concentrations.

In Palestine, certain grape varieties after 9 years of favorable growth began to deteriorate in saline soil, Cl accumulating in the injured leaves and fruits (56). Increasing KCl concentrations depressed wheat and buckwheat growth in solution cultures, whereas increasing NaCl depressed only the root growth (49). Although Cl affects buckwheat harvests, it does not affect those of sunflowers (64). It is more harmful to buckwheat when $NH_4$ rather than $NO_3$ is used (64).

The total concentration of salt was a major factor in the growth depression of peach trees grown in sand cultures (32). At equal osmotic concentrations Cl was more toxic than $SO_4$ and was accompanied by leaf symptoms not occurring with $SO_4$ (32). With certain crops, Cl and $SO_4$ salts on an equal osmotic basis depressed growth equally; in other crops Cl was slightly the more toxic (45). The effect of NaCl on yield reduction in bean fruits was greatest in those treatments in which the soil moisture tensions were greater at the time of irrigation (3). At equal osmotic values very similar amounts of plant growth occurred with NaCl, $CaCl_2$, and $Na_2SO_4$ but with $MgCl_2$ and $MgSO_4$ there was a marked depression as a result of Mg toxicity (22). In solution cultures, Cl partially prevented the toxic effect of iodides on corn (42). According to Eaton (16) there appears to be no threshold concentration below which Cl-sensitive crops are uninjured by NaCl. Growth-depression curves showed no abrupt point at which toxicity became pronounced (17).

Sewage treated with chlorine gas before entering a creek caused a brown discoloration (blighted appearance) of outer leaves in lettuce (65). Advantage is taken commercially of the toxicity of Cl in various combinations: many of the most persistent weeds are eliminated by chlorates (15, 50). Nitrates inhibit much of the toxicity of chlorates (35, 49, 58). Soybean plants have been injured in culture solutions with very low concentrations of chlorate or perchlorate (70). Chlorine-containing organic compounds such as chloropicrin are valuable as soil fumigants (25) which in some cases have brought about increased plant growth (34).

## MORPHOLOGICAL AND PHYSIOLOGICAL EFFECTS OF Cl

Field tests showed tubers of potato fertilized with NaCl to be inferior and to have a bitter alkaline flavor (49). Leaves of high-Cl potato plants in the field and in sand cultures contained lower percentages of total carbohydrates and higher percentages of starch than those of controls (6). High Cl in field-grown potato plants reduced the chlorophyll content to a degree related to their increased water content (49). Excessive NaCl or KCl decreased the Mg content of plants and their chlorophyll content (11).

Low amounts of KCl reduced the symptoms of Mg deficiency in tobacco, and the Cl increased the water content of the plants and their resistance to desiccation "drought spot" (49). An application of 100 pounds or less of Cl per acre may seriously interfere with carbohydrate metabolism in tobacco plants, disturbing the amylolytic activity in the leaf. Excessive starch accumulates in the leaves, which become thickened. Excessive Cl produces muddy leaf colors and injures the toughness and elasticity of the leaves. The adverse effect of Cl

on combustibility is partly due to reduction of the $K_2O$ which may exist in the leaf in combination with organic acids [Garner et al. (49)]. When both the K and Cl contents of tobacco were increased, this unfavorable action of Cl was compensated by the favorable influence of K (13). Tobacco leaf quality may be affected by Cl favorably or not, depending on the amount present, the use to be made of the tobacco, and the stages in handling and manufacturing operations which it has reached.

Wheat, oats, and barley in soil containing NaCl may develop a waxy bloom on the leaf surface and a thickened cuticle. The size of the epidermal cells decreased when injurious concentrations occurred in soil (49). Retardation in height and in the period of blooming, and a reduction in number and size of leaves and nodules occurred in bean plants grown in sand containing as much as 1 per cent NaCl (49).

The physiological response to Cl may be the result of enzyme activation brought about by increased acidity of the plant cells due to the chlorine; too great acidity changes the acceleration to an inhibition of enzyme activity. The addition of Cl to soil increased the Cl content of the plant and the absorption of bases and exerted a favorable action on the water economy (4). The addition of NaCl to nutrient solutions for tomato plants, however, reduced the intake of both water and nutrient ions (44). Sugar beet plants become more succulent with Cl than with $SO_4$ and were better able to withstand wilting (67). As Cl accumulates in buckwheat straw, Ca, Mg, and K also increase (64). Excess Cl absorbed by plants is accompanied by Ca; this disturbs the K/Ca balance and is one cause for the injurious effect of K (47).

In root crops a watery root was induced by Cl (49). In the fruits of grape plants injured in saline soil, glucose was found to decrease, whereas acids increased (56). Hydrogen-ion concentration was increased in the sap of plants by increased Cl (53) but not by $SO_4$ (17).

Anatomic response of the roots of Valencia orange seedlings to high concentrations of Cl and high pH resembles that of dormancy. Frequency and length of root hairs are reduced by high Cl or high pH, which also induces chlorosis and tipburn (31), the most severe symptoms occurring when both Cl and pH effects are combined.

Plants in saline sand cultures showed a higher content of both sugars and starch, suggesting interference of accumulated salts with cellular activities associated with carbohydrate utilization (20).

In the assimilation of N by red kidney beans (68) from NaCl and $CaCl_2$ saline solutions of various osmotic concentrations, there was a linear decrease in green weight with an increase in the osmotic concentration of the substrate. With $CaCl_2$ the plants made as much shoot growth as those with NaCl but less root growth. Increased salts in the medium were associated with decreases in the percentages of $NO_3$-N and protein-N in the plants. With NaCl more N, P, and K were absorbed than with $CaCl_2$ (21). For most salts and mixtures the relationship between growth and osmotic concentration tended to be linear (22). Plants grown in soil containing 0.2 per cent NaCl (dry soil weight basis) had less

starch in their leaves than when grown in nonsaline soil. When soil was dried to near the wilting percentage prior to irrigation, there was a marked progressive depletion of starch in the leaves (69).

SUMMARY

The influence of Cl upon plants depends upon the nature of the plant, the growth medium, and the climatic conditions. Sand and solution cultures have indicated a beneficial effect of Cl for the growth of tomatoes, cotton, buckwheat, and peas. Field tests with potatoes, tobacco, and asparagus have shown improvement in the crops when low concentrations were used. Physiological response to Cl may be the result of slight changes in acidity and of enzyme activation.

Applications of 20 to 30 pounds of Cl per acre increased the production of tobacco. The quality of tobacco may be improved by the use of Cl, for the too rapid burning was corrected by the application of 50 pounds of NaCl or KCl per acre. The Cl content of tobacco was highest in the upper leaves of the plant. Gradients in Cl distribution also occur in avocado leaves and fruits. The Cl content of Nitella cell sap exceeded that of the water medium.

Barley plants accumulate Cl more readily than $SO_4$. Lemon trees were found to be much more tolerant to $SO_4$ than to Cl. There is a wide range in the tolerance of plants to Cl. The age of the plant is an important factor in the degree of toxicity of NaCl. In order to avoid Cl toxicity, the irrigation water for citrus trees should not contain more than 150 to 200 p.p.m. Cl. With certain crops Cl and $SO_4$ salts, on an equal osmotic basis, depress growth equally; in other crops Cl is slightly the more toxic. There appears to be no threshold concentration below which Cl-sensitive crops are uninjured by NaCl. Commercial use is made of the toxicity of certain Cl-compounds especially in weed eradication.

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# COBALT AND NICKEL IN SOILS AND PLANTS

## R. L. MITCHELL

*The Macaulay Institute for Soil Research, Aberdeen, Scotland*

In accordance with their similar ionic radii of 0.82 and 0.78 A, and their common valency of 2, cobalt and nickel are closely related geochemically, and it is convenient to discuss their behavior in soils and plants together. As their atomic weights differ by less than 0.5 per cent (58.94 and 58.69 respectively), comparisons based on percentage values hold also for atomic proportions. The best values for the average content of the earth's crust appear to be about 23 p.p.m. Co and 80 p.p.m. Ni (17). In igneous rocks, mineral lattice replacement of magnesium and to some extent of ferrous iron by cobalt and nickel is the normal mode of occurrence, as is to be expected from their ionic radii ($Mg^{++}$ 0.78, $Fe^{++}$ 0.83). As the parent ferromagnesian minerals such as the olivines, pyroxenes, and amphiboles occur chiefly in the more basic rocks, these rocks contain much more cobalt and nickel than do the more acidic, silica-rich types. Nickel, because of its smaller radius and a covalent bond effect, is concentrated in the early crystallizing ultrabasic types, whereas cobalt follows the magnesium content closely. This is illustrated by the data of table 1, quoted from Wager and Mitchell (26). Generally the nickel content of an igneous rock is greater than its cobalt content, but in the more acidic types the cobalt content may be the greater. The great preponderance of cobalt shown by the ferrogabbros in table 1 is unusual. In some acid rocks, contamination of the magma by country rock may upset the ratio and increase the amounts of both elements above the expected level.

In sediments, the distribution of trace constituents is governed not by ionic radii but by ionic potentials, and in general more cobalt and nickel are found in argillaceous than in arenaceous rocks. Limestones, even when dolomitic, are usually low in cobalt and nickel (below 10 p.p.m.), and therefore the association of these elements with magnesium does not persist into the sedimentary cycle of weathering.

The major ore deposits of cobalt and nickel occur as sulfides, but these are of little importance in soil formation except in their immediate neighborhood.

Such, in brief, is the geochemical and geological background to the study of cobalt and nickel in soils and plants. Total contents of 20 to 100 p.p.m. Co and 50 to 500 p.p.m. Ni, or even higher, are to be expected in soils derived from basic igneous rocks or argillaceous sediments, whereas contents below 20 p.p.m. Co and 50 p.p.m. Ni are normal in soils from sandstones, limestones, and acid igneous rocks. These generalizations are of use when dealing with residual soils or with drifts in areas of uniform geology, although some differentiation as a result of size sorting may be looked for. Where glaciation occurs over areas of complicated geology, a till of mixed origin generally forms the soil parent material and it becomes impossible accurately to anticipate the probable cobalt and nickel content.

Semiquantitative spectrographic determinations on several podzol profiles have shown that there appears to be no accumulation of cobalt or nickel in the iron-rich illuvial B horizon or even in any iron pan that may be present. Quantitative data are not yet available, but the spectral lines of cobalt and nickel show no visual variation in intensity throughout the profile below the organic litter horizons, although the variation in the iron content is very obvious. It may be noted here that all original data in this paper have been obtained spectrographically by the author or by R. O. Scott (6, 13, 20, 21). The concentration of cobalt and nickel in the mineral matter (ash) of organic litter layers of forest soil podzol profiles, already reported by Goldschmidt (8), is confirmed in these studies. It appears to be of the order of ten-fold. In cultivated soils little or no variation in content of cobalt or nickel throughout the profile has been found.

The bulk of the content of cobalt and nickel in soils is bound up in the crystal lattice of minerals and is not readily available to the plant, and comparisons of

TABLE 1

*Contents of cobalt and nickel in a series of rocks of common origin, ranging from ultrabasic to acidic, from the Skaergaard Intrusion, Greenland*

From Wager and Mitchell (26)

| | GABBRO-PICRITE | OLIVINE GABBRO | MIDDLE GABBRO | HORTON-OLITE-FERRO-GABBRO | FERRO-HORTON-OLITE-FERRO-GABBRO | FAVALITE-FERRO-GABBRO | BASIC HEDEN-BERGITE-GRANO-PHYRE | ACID GRANO-PHYRE |
|---|---|---|---|---|---|---|---|---|
| CoO........p.p.m. | 100 | 90 | 50 | 75 | 40 | 4 | 2.5 | 4 |
| NiO........p.p.m. | 750 | 250 | 30 | <1 | <1 | <1 | 4 | 6 |
| MgO......per cent | 27.1 | 9.6 | 5.3 | 5.5 | 1.7 | 0.25 | 1.1 | 0.15 |

total cobalt in the soil with plant uptake have shown little correlation (22). Data for nickel are lacking in the literature.

In an attempt to correlate plant uptake with soil content, extractions with 2.5 per cent acetic acid (pH 2.5), 2.5 per cent acetic acid neutralized with ammonia to pH 4.5, and normal ammonium acetate (pH 7.0) have been made on a series of soils of low to high cobalt and nickel content. Some of the results are given in table 2, together with comparative figures for potassium and magnesium. From the results it is obvious that the cobalt and nickel extracted by 2.5 per cent acetic acid cannot be considered truly exchangeable, as are potassium and magnesium. Nor can we be dealing with the break up of primary ferromagnesian minerals, as there is no increase in magnesium extraction with increasing acidity. It seems that we are dealing with cobalt and nickel adsorptively bound, probably in secondary clay minerals, but more firmly held than the usual exchangeable bases. Renold (15) has shown that heavy metals, including nickel, are more difficult to displace from permutites than are the alkalies and alkaline earths.

The soils of table 2 are typical of northeast Scotland, and the geological origin of the soil parent material has been noted in the table. There appears to be little differentiation in the relative ease of extraction of cobalt and nickel at pH

values between 2.5 and 7.0, the only soil in which the cobalt to nickel ratio varies appreciably at different pH values being that which is very high in nickel. There is, on the other hand, no correlation between the total content and the easily soluble fraction.

In practice, the pH 2.5 extract has proved of use for diagnostic purposes in cobalt deficiency. Table 2 contains two soils that are low in cobalt, four normal, and two rather above normal, the highest being derived from a rock of basic igneous origin.

It is interesting to compare the amounts of cobalt and nickel extracted by 2.5 per cent acetic acid with the amounts taken up by pasture herbage grown on

TABLE 2

*Amounts of cobalt and nickel extracted at different pH values from soils of varying origins*
In p.p.m. air-dry soil

| SOIL AND PARENT MATERIAL | TOTAL | | 2.5 PER CENT ACETIC ACID, pH 2.5 | | | | ACETIC ACID + AMMONIA, pH 4.5 | | NORMAL AMMONIUM ACETATE, pH 7.0 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Co | Ni | Co | Ni | Mg | K | Co | Ni | Co | Ni | Mg | K |
| 11525 Granitic gneiss till....... | 14 | 26 | 1.3 | 1.8 | 56 | 49 | 0.58 | 1.05 | 0.09 | 0.13 | 50 | 51 |
| 11540 Mixed till (contaminated igneous)............... | 11 | 28 | 0.76 | 0.79 | 180 | 64 | 0.41 | 0.33 | 0.07 | 0.07 | 170 | 72 |
| 11560 O.R.S. till (clay)......... | 11 | 27 | 0.60 | 0.69 | 126 | 65 | 0.17 | 0.18 | 0.04 | 0.06 | 96 | 67 |
| 11563 Diorite till.............. | 33 | 230 | 2.3 | 19 | 290 | 41 | 0.97 | 10.3 | 0.21 | 3.8 | 250 | 36 |
| 11591 Mixed till (epidiorite + granite)............... | 21 | 22 | 0.41 | 0.50 | 90 | 100 | 0.14 | 0.14 | 0.03 | 0.02 | 114 | 91 |
| 11597 Mixed till (granite + schist)................. | 14 | 7 | 0.46 | 0.16 | 22 | 39 | 0.16 | 0.07 | 0.03 | 0.01 | 20 | 46 |
| 29146 O.R.S. till (loam)........ | 4 | 13 | 0.26 | 0.60 | 83 | 102 | 0.06 | n.d.* | 0.0 | n.d. | n.d. | n.d. |
| 29152 Quartzose schist drift.... | 1 | 16 | 0.14 | 0.56 | 37 | 32 | 0.06 | n.d. | 0.0 | n.d. | n.d. | n.d. |

\* n.d. = not determined.

the soil. The first six examples in table 3 are from the same district of Aberdeenshire and of about the same pH, and therefore climatic and acidity conditions are excluded from the possible extraneous effects in these instances. From the ratios there is apparently a preferential uptake of nickel rather than cobalt by the plant, and in view of the previously noted constancy of the Co/Ni ratio in soil extracts at differing pH values, it seems probable that this is a true difference caused by preferential uptake by the plant. This is interesting in view of Scharrer and Schropp's finding (18) that in water and sand cultures, small additions of nickel were beneficial to most plants studied (oats, wheat, rye, barley, maize, peas), although depressed yields were obtained with cobalt. A review of other work on this and related aspects is given by Scharrer (19).

The normal content of the dry matter of plant material is from 0.01 to 0.4 p.p.m. cobalt and 0.10 to 5 p.p.m. nickel, depending on the species, part of the plant, stage of maturity at time of sampling, soil content, and soil acidity among other factors. When cereals are grown on soils high in nickel, for instance, very

high contents will be found in the grain. These factors all influence the data of table 3; probably the time of sampling and relative abundance of the pasture species are of greatest importance. The uptake of a few species from a cobalt-deficient soil in pots and from a normal soil in the field are given in table 4 to

TABLE 3

*Cobalt and nickel in soils and in pasture herbage grown thereon*

In p.p.m. air-dry soil and oven-dry plant material

| SAMPLE | ACETIC ACID EXTRACT OF SOIL, pH 2.5 | | PASTURE CONTENT | | RATIO PASTURE/SOIL | |
|---|---|---|---|---|---|---|
| | Co | Ni | Co | Ni | Co | Ni |
| 1 | 0.19 | 0.92 | 0.07 | 2.00 | 0.37 | 2.2 |
| 2 | 0.22 | 0.48 | 0.06 | 1.02 | 0.27 | 2.1 |
| 3 | 0.26 | 0.58 | 0.06 | 0.85 | 0.23 | 1.5 |
| 4 | 0.59 | 1.31 | 0.18 | 3.68 | 0.30 | 2.8 |
| 5 | 0.63 | 1.10 | 0.15 | 2.19 | 0.24 | 2.0 |
| 6 | 0.68 | 1.34 | 0.22 | 3.62 | 0.32 | 2.7 |
| 7 | 0.17 | 0.32 | 0.07 | 0.79 | 0.41 | 2.5 |
| 8 | 0.25 | 0.85 | 0.04 | 0.83 | 0.16 | 1.0 |
| 9 | 0.14 | 0.51 | 0.02 | 0.52 | 0.14 | 1.0 |
| 10 | 0.12 | 0.63 | 0.04 | 0.62 | 0.33 | 1.0 |

TABLE 4

*Uptake of cobalt and nickel by different pasture species*

In p.p.m. oven-dry plant material

| | Co-DEFICIENT SOIL IN POTS | | NORMAL SOIL IN THE FIELD | |
|---|---|---|---|---|
| | Co | Ni | Co | Ni |
| Soil content 2.5 per cent acetic acid.............. | 0.17 | 0.32 | 0.50 | 0.60 |
| Cocksfoot........................................ | 0.08 | 0.80 | 0.08 | 0.48 |
| Timothy.......................................... | 0.10 | 0.48 | 0.03 | 0.46 |
| Rye grass........................................ | 0.16 | 1.30 | 0.07 | 0.53 |
| Red clover....................................... | 0.21 | 0.91 | 0.19 | 1.91 |
| Alsike........................................... | 0.30 | 1.48 | | |
| Chicory.......................................... | 0.23 | 1.27 | | |
| Crested dogstail................................. | 0.14 | 0.89 | | |
| Rough-stalked meadow grass...................... | 0.10 | 0.98 | | |

illustrate the effect of different species, already pointed out (11) in New Zealand work.

It is seen that the relative uptakes of the different species vary under the differing conditions of growth, and it is also obvious that the ratio of clovers to grass must control the cobalt and nickel content of the herbage to a considerable extent. Apart from early work of Bertrand and his collaborators (3) and some data given by Kidson and Maunsell (11), cobalt determinations have concen-

trated on the contents in pasture herbage, because of the occurrence of widespread deficiency diseases of sheep and cattle. These diseases were at first ascribed to iron deficiency and cured by feeding impure iron salts and minerals such as limonite. Lines (12) in South Australia appears to have been the first to indicate the essential nature of cobalt in the nutrition of sheep, although the study of similar wasting diseases of sheep and cattle in Western Australia (25) and New Zealand (1) was independently leading to the same conclusion. Since then curative effects of cobalt in similar complaints have been reported from numerous countries (4, 5, 10, 14, 23). In Florida, particularly, the problem has been studied in cattle. Copper deficiency is occasionally also present and may complicate the diagnosis.

In sheep the symptoms of cobalt deficiency are progressive debility: growth is retarded, soon after weaning the lambs appear stunted and unthrifty, wool becomes broken, serous discharge from the eye is common, emaciation and weakness progress until the animal is unable to rise and then it usually dies (24). Some secondary worm infestation may be present. The precise role of cobalt in animal nutrition is not yet established.

Cure can be effected by dosing with cobalt salts, by feeding cobaltized salt licks, or by transfer to a healthy pasture. The last practice was common in certain areas of Scotland before the reason was appreciated. It now appears that herbage contents of above 0.08 p.p.m. Co are necessary to ensure complete animal health. Below this, there is a transition range from about 0.05 to 0.08 p.p.m. where trouble may or may not occur, depending possibly on factors such as amount eaten and its digestibility. Below 0.04 p.p.m. it is unlikely that a healthy permanent sheep stock can be carried. These values refer to samples taken during the spring and summer period, when the herbage is growing, and not to samples taken in autumn and winter.

As difficulties occur in sampling herbage because of variations due to the above reasons and because of soil contamination (which may be responsible for the transition range), a soil determination is more convenient, and it has been found that in the arable cobalt-deficient areas of Scotland, 2.5 per cent acetic acid generally extracts less than 0.25 p.p.m. cobalt, whereas for healthy soils the value is above 0.3 p.p.m. Areas of low cobalt content have been found where no animal trouble has been reported but on which permanent stock is not kept. It is possible that difficulties would arise if these areas were permanently pastured.

The occurrence of cobalt pining in affected areas can be prevented by topdressing the soil with a cobalt salt admixed in a phosphatic fertilizer (23) or with cobaltized superphosphate (2), generally at the rate of about 2 pounds of cobalt salt per acre. This small dressing (about 0.25 p.p.m. Co) is effective for at least one season and in some instances has held the cobalt content of the herbage above the deficient level for at least three seasons (table 5). The duration of the effect probably depends on the soil texture, drainage, and acidity, and on the properties of its colloidal fraction. On a limed soil the effect is less persistent than on one that is more acid, as shown by the data in table 5 for the portion of the granitic loam limed at the end of the first season.

The diagnosis of cobalt deficiency by 2.5 per cent acetic acid extraction is unsatisfactory on soils top-dressed with cobalt, and also on shell sands with free $CaCO_3$, on which cobalt deficiency is found in the western islands of Scotland, as well as in South Australia. The drawing of representative samples of soils carrying permanent pasture is difficult, especially on hill-land.

There is no conclusive evidence of any similar nickel deficiency in stock, although Dixon (7) has found some slight response to nickel, as well as cobalt, at

### TABLE 5
*Effect of top-dressing with 2 pounds CoCl₂·6H₂O per acre on the cobalt content of pasture herbage over three seasons*

In p.p.m. oven-dry plant material

| SOIL | pH | COBALT ADDITION | 1ST SEASON | 2ND SEASON | 3RD SEASON |
|---|---|---|---|---|---|
| O.R.S. loam.............. | 5.7 | No Co | 0.05 | 0.08 | 0.05 |
| | | 0.25 p.p.m. Co | 0.62 | 0.22 | 0.05 |
| Granitic loam........... unlimed............... | 5.9 | No Co | 0.13 | 0.09 | 0.07 |
| | | 0.25 p.p.m. Co | 0.68 | 0.37 | 0.28 |
| Granitic loam........... limed................. | 6.5 | No Co | .... | 0.08 | 0.07 |
| | | 0.25 p.p.m. Co | .... | 0.15 | 0.08 |

### TABLE 6
*Nickel contents of an infertile and an adjoining fertile soil from Aberdeenshire*

| SOIL | DEPTH | TOTAL Ni | ACETIC-ACID-SOLUBLE Ni | AMMONIUM-ACETATE-SOLUBLE Ni |
|---|---|---|---|---|
| | *cm.* | *p.p.m.* | *p.p.m.* | *p.p.m.* |
| Fertile | 5–30 | 410 | 11 | <3 |
| | 30–40 | 660 | 4 | <3 |
| | 70–80 | 870 | 11 | 8 |
| | 100–110 | 810 | 13 | 8 |
| Infertile | 5–25 | 720 | 86 | 23 |
| | 25–35 | 830 | 27 | 20 |
| | 60–70 | 540 | 57 | 39 |
| | 100–110 | 710 | 57 | 41 |

Morton Mains, New Zealand. The importance of nickel is due rather to its poisonous effect on crops. Haselhoff (9) has reported the ill effects of effluent water from a nickel ore crushing plant. In small areas in Aberdeenshire, soils occur with more acetic-acid–soluble nickel than potassium and, on these, crops fail until they are liberally dressed with lime. Cereals on these soils display striping typical of heavy metal chlorosis, and crops grown on the infertile sections after liming contain up to 50 p.p.m. nickel. The soils, derived from basic igneous rocks and having had at least at some stage an organic surface layer, show about 500 p.p.m. total nickel and 100 p.p.m. acetic-acid–soluble nickel in their infertile

patches, whereas adjoining fertile areas have a similar total content not more than 11 p.p.m. acetic-acid–soluble nickel.

In table 6 data for the total, acetic-acid–soluble, and ammonium-acetate-soluble nickel are given for profiles from the infertile area and a closely adjoining fertile area.

Some easily soluble copper is also present but the chromium is not abnormal. It is possible that nickel may be the limiting factor in the infertile soils described by Robinson, Edgington, and Byers (16). Although cobalt is as poisonous to plants, there is no evidence of sufficient occurring naturally to give rise to ill effects; experimental dressings of 80 pounds of a cobalt salt per acre have shown some reduction in growth of herbage.

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# COPPER AND PLANT GROWTH

ANNA L. SOMMER

*Alabama Agricultural Experiment Station*

Various reports of the stimulating effect of copper for plant growth, usually in connection with the use of bordeaux mixture, appeared during the latter part of the last and the early part of this century. These reports have been reviewed by Lutman (36) and Cook (14). In them the essentiality of copper, and therefore the possibility that the stimulating effect might be due to a deficiency of this element in the soils, was apparently not considered.

After experiments with dieback of citrus extending over a number of years in which beneficial results were obtained by applications of copper sulfate to the soil and bordeaux mixture as a spray, Floyd (22) in 1917 recommended these treatments as preventives and cures of the disease. Since then applications of copper salts to the soil have been found to cure dieback (exanthema) in olives (49), avocados (45), and various deciduous trees including pear (2, 41, 49), peach (2), plum (2, 12), apricot (2), apple (2, 20, 49), and tung oil (19).

Applications of copper sulfate were also found to cure "reclamation" disease of cereal grains occurring on peat soils in Europe. The disease has been found in various parts of the world, and is called "Urbarmachungskrankheit," "Heide-moorkrankheit," "Ontginngszeitke," "Gulspids," "yellow tip," and "wither tip"—the name depending chiefly upon the country and describing the symptoms of the disease or the soil in which it occurs.

In 1927 Felix (21) found that the addition of copper sulfate made possible the growth of onions and lettuce on unproductive peat soils in New York, and Allison, Bryan, and Hunter (1) obtained striking results with many crops on the saw-grass soils of the Florida Everglades by fertilization with this compound. Beneficial results on these newly cultivated soils were also obtained by other treatments, particularly manganese sulfate, manure, and unslaked lime. Results with copper sulfate, however, were usually by far the best, and investigators began to suspect that copper was necessary for plant growth and that soils responding to such treatments were deficient in this element.

## SOLUTION CULTURE WORK

Early experiments with solution cultures failed to show that copper was essential because the amount necessary for plant growth is very small and relatively small amounts are toxic. Thus, Brenchley (9) found only toxic effects when copper was added to solution cultures. The satisfactory growth of plants in solutions without the addition of copper was due not only to the minute traces of this element occurring as an impurity in the salts used in relatively high concentrations, but also to the traces of copper in the distilled water, since most of the water used was from copper stills. The first conclusive evidence that copper was essential for plant growth was the result of experiments by the author (51, 52) in which specially purified salts were used and the water for the culture

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solutions was redistilled from pyrex. Tomato, sunflower, and flax plants showed the effects of copper deficiency in the early stages of growth, whereas flax, in an earlier unpublished test where water from a copper still was used, showed no response to copper until the fruiting stage was reached. Considerable solution culture work has been done in the last 15 years showing the necessity of this element for the growth of various plants—tomatoes (4, 5, 43, 44, 51, 52), barley (34), oats (8, 43, 57), wheat (43), flax (43, 52), *Lolium sublatum* (43), lucerne (43), peas (43), *Phalius tuberosum* (43), subterranean clover (43), sunflowers (51, 52), beets (57), and plums (28). There now appears to be ample proof that copper must be included in the list of those elements necessary for plant growth.

Evidence that reclamation disease of grain crops was due to the lack of available copper was obtained by Brandenburg (8), who compared the symptoms of oat plants grown in newly cultivated peat soil with those caused by copper deficiency in solution cultures. Piper (43) found the symptoms of oats grown on a copper-deficient sandy soil in Australia to be the same as those produced in culture solutions deficient in this element; plum trees grown by Hoagland (28) in copper-free solutions showed symptoms of dieback or exanthema.

### SYMPTOMS OF COPPER DEFICIENCY

As in the case of all deficiencies, that of copper under field conditions cannot always be detected by typical symptoms. In the first place, there are varying degrees of deficiency, from those causing only a slight decrease in yield to those allowing almost no growth. Among different types of plants, symptoms vary greatly; among plants of the same family, and even in the same plant under different conditions or in different varieties, symptoms vary to a considerable degree. Thus Anderssen (2), first to conclude that dieback disease was due to copper deficiency *per se* and reporting characteristic rosetting for peaches, plums, apricots, and apples, wrote: "Pears do not show a rosetting but the tips of the apical leaves merely become badly scorched, resulting in dieback." Oserkowsky and Thomas (41), on the other hand, reported stimulation of the axillary buds after the death of the apical growing points and a subsequent witches'-broom appearance. Anderssen stressed the chlorosis part of the picture for most trees studied, and his observation that pear trees do not very often exhibit chlorosis agrees to some extent with that of Oserkowsky and Thomas, who reported that "chlorosis as a symptom of exanthema in pears could not be observed."

The most characteristic symptom of exanthema or dieback is the death of the young growing tips, after which, in many cases, axillary buds below the dead part are stimulated and produce a bushy growth, or rosetting. Some kinds of trees, and others only at certain times, show chlorosis. Chlorosis is more often confined to the older leaves. Occurring sometimes with the disease are hard fissures in the bark with gum pockets. Floyd (22) gave as primary symptoms of dieback of citrus the formation of gum pockets, stained terminal branches, marked or ammoniated fruit, bark excrescences and multiple buds; as secondary symptoms, exceptionally dark green color of foliage, distorted growth of immature angular terminal branches, frenching of foliage, and leaves that are long in relation to their width.

When severe enough to be classed as reclamation disease, symptoms of copper deficiency of cereal grains are characteristic. The withering and graying of the tips, which are responsible for several of the names of the disease, are the symptoms most often mentioned. There is also a bending, loss of turgor, turning backward of leaves, and a dying of the tips of newly emerging leaves.

The appearance of copper-deficient plants, other than those falling in the aforementioned groups, varies considerably. Although some investigators stress chlorosis as a symptom of copper deficiency, there are certain plants for which this cannot be considered a characteristic symptom. A notable example is the tomato. The results of the author agree with those of Arnon and Stout (4) and Reed (44). In solution cultures, copper deficiency is characterized by stunted growth of both roots and tops, dark bluish-green foliage, and a failure to produce flowers. Considerable curling of the leaves is also evident. Bailey and Mc-Hargue (5) mentioned chlorosis under certain conditions, but did not include it among the characteristic symptoms. Chlorosis occurring under field conditions where copper is deficient may be due to complicating factors, particularly in peat soils. Thus Teakle, Morgan, and Turton (55) obtained the stunted growth and characteristic curling of the leaves on one field when no copper was applied; on another, without copper, the plants made very little growth and developed small bunchy tops with yellow, unhealthy leaves. These investigators thought the difference probably due to the difference in soils, including high calcium carbonate content and manganese deficiency in the soil producing the smaller chlorotic plants.

Chlorosis was not observed by the author when flax or sunflowers were grown in copper-deficiency solutions, but Piper (43) reported that the upper leaves of flax turned yellow and died as the growth ceased.

Among plants described, but for which the author has found no report of chlorosis in copper deficiency, are lucerne (43), peas (43, 55), carrots and peppers (23).

Chlorosis (leaves pale green, mottled with yellow, yellow to white) was noted for the following: subterranean clover (43), currants (56), eggplant, celery, onions (23), corn (55), beets (57), and lettuce (21, 23). Excellent photographs showing the effect of copper deficiency for oats, wheat, *Lolium sublatum*, flax, tomatoes, and lucerne were presented by Piper (43). Forsee (23) also presented photographs of a number of plants (peppers, eggplant, carrots, cabbage, celery, lettuce, and onions) grown with and without copper.

## COPPER DEFICIENCY IN SOILS

Soils high in organic matter, particularly newly cultivated peat soils, are those most frequently discussed in connection with copper deficiency. The occurrence of such soils in Europe and the eastern part of the United States has been shown on maps by Rademacher (48). Copper deficiency has been reported for many other soils, especially of the sandy and gravelly types. In discussing malnutrition symptoms and treatment of citrus (Florida), Bryan (11) wrote: "... copper deficiency is known to occur on most any soil type, it is more prevalent on acid soils with clean cultural practices than on neutral soils and types with

plenty of cover crop." Copper deficiency on sandy and gravelly soils has been found over considerable areas in Australia (43, 54), South Africa (2), and to a less extent in various other countries.

Much more copper is necessary for the correction of copper deficiency in soils of high humus content than in other soil types, and increases in yield may be obtained on heavy soils with amounts which would be toxic if applied to lighter soils. In pot experiments with soil of the Florida Everglades, Bryan (10) obtained good response with copper sulfate used at the rate of 250 pounds per acre. Manns, Churchman, and Manns (37) obtained increases in yield with applications up to 300 pounds on heavier soils but found that 150 pounds per acre decreased yields on the lighter soils. Wild and Teakle (58) reported that bluestone applied at the rate of 10 pounds per acre to very sandy or gravelly soil proved harmful, and plots receiving $2\frac{1}{2}$ pounds per acre gave best results. They recommended 5 pounds per acre for the first year as general practice for cereals, and suggested that smaller amounts might be adequate for subsequent crops. Hill and Bryan (27) found that copper toxicity was greatest in soils with least buffer capacity, and also that the toxic properties decreased with an increase in time after application.

There is evidence to indicate that the beneficial effect obtained by the addition of copper sulfate to raw peat soils is not due simply to the increase in soluble copper available for absorption by the plant. Allison, Bryan, and Hunter (1) found that the application of manganese sulfate and some other substances gave beneficial results, though not so good as were obtained by the use of copper sulfate, in correcting the unproductiveness of the Florida Everglades soils. Moreover, Bryan (10) obtained good growth with manganese sulfate solution applied to leaves or to leaves and stems of plants in these peat soils when growth of untreated plants was very poor. In his studies of reclamation disease in Holland, Smith (50) found that sterilization of the soil did not prevent the disease, but when soil which caused this disease was added to a normal sandy soil oat plants showed symptoms of reclamation disease. He isolated an organic substance which he called "Gliedine," a few milligrams of which produced symptoms of reclamation disease on normal pea and oat plants. He concluded that the beneficial effect of copper on soils producing plants with reclamation disease was due to the formation of an insoluble compound of copper and the Gliedine. This does not, however, explain the results of Brandenburg (8) and others who later obtained the symptoms of reclamation disease in copper-free solutions to which no toxic organic substance had been added, unless it is assumed that the toxic effect is due, at least in part, to the precipitation of copper by the Gliedine and which may take place within as well as outside the plant.

## EFFECT OF COPPER ON CULTURE MEDIA

Copper appears to play a part in the oxidation-reduction system of the medium in which the plant is grown. Arnon (3) found that the addition of copper to solutions without forced aeration greatly improved the growth of barley plants when ammonium salts were used as the source of nitrogen. According to Willis

and Piland (59), the addition of copper to a soil may be beneficial or not, depending on the oxidation intensity of the iron and manganese content. They reported that in preliminary tests copper sulfate increased potentials when air was present, but that there was a decrease when air was excluded from the soil. They found that the addition of copper sulfate to certain unproductive peat soils would sometimes cause a chlorosis which could be overcome by external applications of ferrous sulfate solution. Chapman, Liebig, and Vanselow (13) found that copper in nutrient solutions would sometimes cause iron chlorosis. They suggested that the action of copper (as well as that of zinc and manganese) may be through reactions affecting the oxidation of iron and hence its absorbability by the plant roots or transport through the plant. In work on the essentiality of copper, the author also had difficulty at times in keeping the growing parts of the plant green when this element was included in the solutions, but attributed the difficulty to the rapid growth of the plant and the precipitation of the iron.

Further evidence of the effect of copper on iron absorption by, and possibly the distribution within, the plant may be found in the data of Anderssen (2). Although he makes no mention of the fact, examination of the data presented in a table giving the results of analyses of leaves, wood, and bark from normal and chlorotic trees (on the basis of dry material) shows a negative correlation between the amounts of copper and iron for the top, middle, and lower leaves; wood and bark for the current, 1-year- and 2-year-old growth; and for the 3-year-old bark. There are more copper and less iron in the normal than in the chlorotic plants in all except the 3-year-old bark, where the relationship is reversed.

### FUNCTIONS OF COPPER WITHIN THE PLANT

Probably the most frequently suggested function of copper in plant metabolism is that of chlorophyll formation. A number of investigators have reported increases in chlorophyll content after applications of copper. Two striking examples will be cited: Bergman and Truran (7) found that the leaves of cranberry plants which had been sprayed twice with bordeaux mixture had 15 per cent more chlorophyll by weight than unsprayed leaves, and that the chlorophyll content did not begin to decrease as early in the fall as it did in unsprayed plants. Orth, Wickwire, and Burge (40) reported 4.6 times as much chlorophyll in leaves of orange trees that had been fertilized with copper sulfate as in those of untreated trees. In this case the trees receiving no copper made very little growth as compared with good growth of trees fertilized with this element.

The fact that certain plants cease to grow as a result of copper deficiency and still show no signs of chlorosis is evidence that either the role of copper in chlorophyll formation is indirect, or that some other function is sooner or more seriously affected. Further evidence along this line may be found in the work of Bailey and McHargue (5). Where tomato plants were grown in copper-deficient media, they found that necrotic lower parts contained more copper than did young growing parts of nonchlorotic plants.

Another explanation of the greater amount and longer persistence of chlorophyll in copper-treated plants, as reported by Bergman and Truran, is the possi-

bility of a protective effect of copper against the destruction of chlorophyll. Thus, according to Lutman (36): "The difficulty experienced in extracting chlorophyll from sprayed plants has already been noted by Ewert. The copper salts evidently enter into some sort of chemical union with the chlorophyll, forming a substance which is very tenacious in its hold on the proteid substratum of the chlorophyll bodies and which renders the coloring matter more stable in the presence of sunlight." He suggested a more intense sunlight in continental United States as the explanation of why increased yields of potatoes are obtained here and not in Germany by the application of bordeaux spray when its use as a fungicide or insecticide is not necessary. The protective action of copper against the destruction of chlorophyll is also borne out by the work of Anderssen (2), who grew wheat seedlings in solutions with and without copper for 10 days in the light and then put them in a dark cupboard for a week. He reported that, on removal from the dark, plants in solutions to which copper had been added were distinctly greener than those in solutions without this element.

The most fertile field of research concerning the function of copper has been that of enzymes. Stotz, Harrer, and King (53) found evidence that the catalytic effect of certain plant juices on the oxidation of ascorbic acid was due in part to copper-protein catalysts, and Kubowitz (33) in 1937 purified a copper-protein (a polyphenol oxidase) from potato juice. Since then, catalytically active copper-proteins from a number of plant sources have been purified (15, 16, 17, 30–32, 42). These copper-protein complexes show considerable specificity (30, 35, 38). According to Ball (6): "Oxidative enzymes containing copper may be divided into 2 groups according to their substrates. One group would thus contain those enzymes which oxidize mono- or polyphenols; the other, whose substrate is ascorbic acid." Both appear to oxidize their substrates by means of change of copper from the cupric to the cuprous form, the latter being oxidized by oxygen.

Giri (24) found an inhibition of soybean phosphatase activity by vitamin C copper-protein complex that was annulled by glutathione, cystine, cysteine, and various inorganic reducing agents. The rate of oxidation of the vitamin appeared to control the degree of inhibition, and he concluded that: ". . . the regulation of phosphorus metabolism in plants by the interaction of phosphatases, vitamin C and glutathione in the sense of hydrolysis on one hand and synthesis on the other possess physiological significance." Further evidence of a relationship between ascorbic acid (and therefore the possibility of a copper-protein ascorbic acid oxidase also) and phosphorus metabolism was found by James, Heard, and James (29). They showed that additions of ascorbic acid to barley sap, plus hexosediphosphate, increased the loss of hexosediphosphate and the gain of unhydrolyzed esters (triosephosphates), and that the addition of hexosediphosphate caused oxygen consumption only if ascorbic acid was present. Although they found that the addition of copper ion irreversibly oxidized the ascorbic acid, a copper-protein oxidase may be a part of the enzyme system in the living plant and thus play a part in respiration.

Since it has been shown by Goddard (26) that cytochrome C of wheat germ has the same absorption spectrum as heart cytochrome C and is oxidized by heart

or wheat cytochrome oxidase, it seems probable that a function of copper in the plant comparable to that found by Schultze (46, 47) in the animal (rat) may be demonstrated. Schultze found copper necessary for the formation and maintenance of cytochrome oxidase of heart and liver tissue and of bone marrow. He demonstrated that the oxidase activity of bone marrow, greatly reduced by a copper-deficient diet, could be restored to maximum within 24 hours.

Neish (39) found a greater percentage of copper in the chloroplasts than in the whole leaf. In *Brifolium pratens* the proportion was 74.6 per cent of the total for the whole leaf. He made a point of his findings that iron, copper, and catalase (oxidative catalysts) are concentrated in the chloroplasts, and suggested that this indicates active respiratory processes therein.

With evidence of a positive correlation between chlorophyll and ascorbic acid content in leaves and the presence of ascorbic acid in the chloroplast [Giroud *et al.* (25) and Dischendorfer (18)] it may be suggested that at least one rôle of copper in chlorophyll formation may be that of a part of an enzyme system maintaining normal conditions of the chloroplasts and surrounding tissue. Although a direct catalytic effect of copper on chlorophyll formation is not ruled out thereby, it would be sufficient to explain the chlorotic condition of many plants under copper-deficient conditions.

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# FLUORINE IN SOILS, PLANTS, AND ANIMALS

## H. H. MITCHELL AND MARJORIE EDMAN
### *University of Illinois*

Fluorine is a minor element in the plant and animal kingdoms in the sense that, with few exceptions, it occurs in minute amounts in vegetable and animal tissues. It is of minor importance also because it has not been found to have any well-defined function in living matter. No definite deficiency symptoms have been observed in plants or animals subsisting on a food supply containing the merest trace of fluorine. The element is of importance in plant, and particularly in animal, nutrition because of the harmful effects that it may exert when ingested even in homeopathic doses. Like many toxic substances, however, it may exert a favorable effect on some tissues when ingested in amounts not exceeding a certain very low level.

## FLUORINE IN ROCKS, SOILS, AND WATER

Fluorine is widely distributed in rocks, soils, and waters, particularly in association with phosphorus as fluorapatite, and with calcium as the fluoride (fluospar). It also occurs in nature as cryolite, an impure double fluoride of sodium and aluminum, $Na_3AlF_6$, and in combination with silicates as topaz, tourmaline, the micas, etc. (5). The association of fluorine with phosphates is particularly significant in plant and animal nutrition. Fluorine contributes to the insolubility of phosphate deposits and seems to be essential to their preservation in the soil through the ages. Fluorine provided by volcanic activity serves this purpose, and in this connection, according to Mansfield (35), it is significant that volcanic activity on a considerable scale occurred at approximately the same time as the deposition of the primary phosphates in the United States. Goldschmidt (12) estimated that the earth's crust contains, per ton, 270 gm. of fluorine and 786 gm. of phosphorus. The fluorine to phosphorus ratio in the earth's crust is thus about 0.343 to 1, not much greater than that in many deposits of phosphate rock (36). In such deposits there is a close positive correlation between the content of phosphorus and that of fluorine, the ratio of the two being roughly 4 to 1.

The fluorine in soils originates from the rocks which are the parent substances of most of the mineral components of soils, from the plant and animal debris that supplies the organic matter of the soil, and from the rain water falling upon it. MacIntire and others (33) have estimated the fluorine contribution to the soil from rain water in a locality in Tennessee where the consumption of coal was high as amounting to 0.15 pound per acre annually. On arable land, important sources of soil fluorine are the phosphatic fertilizers used to maintain the fertility of the soil.

Published analyses of the fluorine in soils are few and reveal the expected variability. McHargue and Hodgkiss (27) reported a few, and MacIntire *et al.* (33) a few more. From the former report, a red clay subsoil was found to con-

tain 45 p.p.m. of fluorine, and two lysimeter soils submitted by the Tennessee Agricultural Experiment Station contained 83 and 411 p.p.m. MacIntire and associates reported 93 p.p.m. of fluorine for a fine sandy loam, and from 80 to 338 p.p.m. for various samples of silt loam.

According to MacIntire and associates (33), the relatively insoluble calcium fluoride is the fluorine combination to be expected in soils: "Almost invariably calcium is the dominant exchangeable base and precipitative ion in the soils of humid areas. Conversion to calcium fluoride, therefore, will be the fate of the other fluorine compounds introduced into the soil by phosphatic fertilizers, slags, spray residues, gaseous and solid emissions from manufacturing operations, and rain water." The conditions facilitating the reaction of tricalcium phosphate with calcium fluoride to form fluorapatite have been considered by MacIntire (32). This reaction is of importance in plant nutrition, since to the extent that it occurs, the availability to the plant of phosphatic fertilizers is depressed. The reaction is accelerated by a high pH in the reaction medium.

The fluorine content of sea water ranges from 1 to 1.4 p.p.m. and is a function of the dissolved salts or chlorinity, according to Thompson and Taylor (52). It increases with depth until approximately uniform conditions of salinity prevail. The fluoride-chlorinity ratio is $7.0 \times 10^{-5}$, according to these authors, and is somewhat higher for surface coastal waters and for some waters of straits, channels, and estuaries.

The fluorine content of rain water will obviously depend upon atmospheric conditions with reference to the presence in the air of fluorine-containing gases and dust particles. Industrial and volcanic contamination of the air would be the determining factor.

Fluorine is widely distributed in drinking water in this country and throughout the world. Few waters can be found, according to Nichols (42), that do not contain as much as 0.05 p.p.m. of the element, and concentrations up to 14 p.p.m. have been reported in the United States. The waters more heavily contaminated with fluorine are obtained from deep wells, and the fluorine appears to originate, not from leachings from surface zones, but from deep-seated rock formations "where the gaseous exhalations have been retained under pressure, and are commonly regarded as of pneumatolytic origin" (5). Waters from rivers in the rock-phosphate regions of Tennessee are not abnormally high in fluorine (33), the fluorine content averaging 0.2 p.p.m. (range 0.0 to 0.7 p.p.m.), and in North Africa, domestic water supplies in areas characterized by phosphatic soils were found to contain inappreciable concentrations of fluorine (10).

## FLUORINE IN PLANT NUTRITION

No evidence has been found in the literature indicating that fluorine performs any essential function in plant nutrition. Furthermore, the fluorine content of the plant, with the exception of the roots, is not readily affected by the fluorine content of the soil upon which it grows. Only when the roots contain relatively large amounts of fluorine are appreciable concentrations found in the tops (1).

Machle and associates (28) found no correlation to exist between the fluorine

content of food plants grown in Arizona and the fluorine content of the respective local water supply. Neither Hart, Phillips, and Bohstedt (14), nor MacIntire *et al.* (33) were able to detect any increase in the fluorine content of plants induced by fertilization of the soil with phosphates and slags carrying fluorides. The former investigators observed a particularly high fluorine content in drainage water from a single series of lysimeters in Chickamauga soil at Knoxville, Tennessee, treated with rock phosphate or superphosphate.

The incorporation of soluble fluorides into the soil exerts a definitely toxic effect upon seed germination and plant growth (7, 40, 54), but only when the fluoride concentration reaches a fairly high level (1, 2). Calcium fluoride, the form to which the more soluble fluorides are reduced in the soil, seems to be quite innocuous to plants[1] (33), even when present in the soil in very high concentrations. Somewhat similar results with natural cryolite have been reported by Scott and Karr (49).

The availability to the plant of the phosphorus in phosphatic fertilizers was found by Bartholomew (1) to be inversely correlated with the fluorine contents of the fertilizers. MacIntire and Hatcher (32) have confirmed this observation and have developed a concept of the factors involved in the formation of fluorapatite in the soil. The conversion of tricalcium phosphate to fluorapatite results in a marked decrease in the citrate-solubility of the contained phosphorus. In a later publication (34), MacIntire and others showed that a quenched rock phosphate fusion carrying not more than 0.4 per cent fluorine and of a fineness less than 50 mesh "is a satisfactory fertilizer for *incorporation* with neutral soils, those mildly acidic, and those limestoned or dolomited to the extent that assures the growing of red clover."

### OCCURRENCE OF FLUORINE IN PLANT FOODS

McClure (26) has tabulated the results of fluorine analyses on food materials obtained by reliable chemical methods and published prior to June, 1938. Other information on the fluorine contents of foods has been published by Machle, Scott, and Treon (28), Lockwood (25), and Cheng and Chou (4).

These analytical data testify to the wide distribution of fluorine in plant tissues. Very few foods contain less than 0.1 p.p.m. of fluorine on the fresh basis, and few foods uncontaminated with the residues of insecticidal sprays and fluoriniferous soils and dusts contain more than 2 p.p.m. Tea leaves, containing from 9 to 400 p.p.m. of fluorine on the air-dry basis, are a prominent exception to this statement. A number of analyses of grains and forage crops from fluorite areas indicate much more than the usual concentrations of fluorine, but surface contamination with soil dust is to be suspected in such cases. Contamination from cryolite and fluosilicate sprays may be found on certain fruits and vegetables treated for the control of insect pests. For the sale of such foods in interstate commerce, the maximum chlorine content permitted is 2.8 p.p.m., and for apples and pears 7 p.p.m.

[1] De Turk, E. E. Unpublished data.

### DISPENSABILITY OF FLUORINE IN ANIMAL NUTRITION

Though various essential functions of fluorine in the animal body have been proposed (37), convincing evidence of their reality has not been forthcoming. The usual intake of fluorine in this country outside of areas of endemic fluorosis seems to be about 1 mgm. daily (29), with no suspicion that health or nutriture is adversely affected. Attempts to raise laboratory animals (rats) on rations containing extremely low concentrations of fluorine have been uniformly successful.

Sharpless and McCollum (50) obtained as good growth and reproduction on a largely synthetic diet, containing purified ingredients and ingredients very low in fluorine according to the colorimetric method used in its determination, as on the same diet to which 10 p.p.m. of fluorine was added. No abnormalities in tooth and bone structure or composition, except low fluorine content, were observed on the low-fluorine diet.

Evans and Phillips (9) reared five generations of rats on a mineralized milk diet containing 1.6 p.p.m. of fluorine, with as good results as were obtained on the same diet supplemented with sodium fluoride. On the basal diet, the young rats contained 10.6 to 12.0 p.p.m. of fluorine at birth, and the skeletons of the adult rats contained 8 to 16 p.p.m. of fluorine. The authors of the report concluded that, if the rat possesses a requirement for fluorine, the requirement must be less than 50 $\gamma$ per kilogram of body weight daily.

Lawrenz[2] carried 14 pairs of albino rats through a feeding period of 207 days in a comparison of the nutritive value of diets containing 0.47 and 2.50 p.p.m. of fluorine on the air-dry basis. The rats were produced from mothers which had, themselves, subsisted on a low-fluorine diet. They contained at birth only 0.8 p.p.m. of fluorine, compared with a fluorine content of 5 to 7 p.p.m. of young produced on a stock diet of natural foods. The rats on the two diets exhibited no appreciable or significant differences in rate of growth, dry weight of skeleton, or dry weight of teeth. The total fluorine retained averaged 0.210 mgm. for the rats on the basal diet and 1.648 mgm. for the rats on the supplemented diet. On the basal diet, the average concentration of fluorine in the dry defatted skeleton was 15 p.p.m., in the dry teeth 15 p.p.m., and in the soft tissues in the fresh condition 0.12 p.p.m. For the rats on the supplemented diet, these averages were, respectively, 117, 80, and 0.25 p.p.m. No abnormalities were detected in the teeth of four of the rats on the basal diet that were examined by Dr. Isaac Schour, of the College of Dentistry, University of Illinois, although it must be admitted that the teeth were not fixed in formalin as soon after death as they should have been for the most effective examination. The experiment revealed no signs of malnutrition in the rats on the basal diet, receiving a total of 0.88 mgm. of F in 207 days, equivalent to 27 $\gamma$ per kilogram of body weight daily.

### METABOLISM OF FLUORINE IN THE ANIMAL BODY

Machle, Scott, and Largent (29) observed that an adult human subject on a daily intake of 0.5 to 1.5 mgm. of fluorine excreted through feces and urine as

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[2] Lawrenz, M. Unpublished experiments.

much fluorine as he ingested, within the limits of error of the balance experiment extending over 7 to 20 weeks. Eighty per cent of the excretion appeared in the urine. In these experiments the fluorine was derived entirely from foods and water. When a normal dietary supply of fluorine is supplemented with 6 mgm. daily as sodium fluoride, calcium fluoride, cryolite or bone meal, however, considerable storage of the element will occur (30), varying with the amount of fluorine absorbed. When the absorption of fluorine was measured by the difference between intake and fecal excretion, the percentages of absorption of the fluorine in the forms studied were as follows: sodium fluoride in solution 97, calcium fluoride in solution 95, basal food fluorine 82.5, cryolite in solid form 77, calcium fluoride in solid form 62, bone meal 37. From these values the authors conclude that "the absorption of fluorine is dependent upon the aqueous solubility of the fluoride salt and its state at the time of ingestion." This is not true of other minerals, such as calcium salts, and the evidence in this case is obscured by variations in water and calcium intakes and possibly in the nature of the basal diet. An interesting feature of this study of fluorine metabolism at relatively high levels of intake is the observation that, under the conditions imposed, approximately half of the fluorine absorbed, regardless of the type of salt used, was retained in the body.

A balance study, of course, affords no information as to the tissues in which fluorine storage occurs. From the known affinity of apatite for fluorine and from the probable apatite structure of the main mineral component of bones and teeth, one might infer that these tissues would avidly combine with absorbed fluorine, much more so than would the soft tissues. Limited experimental evidence from human bones and teeth prove that the fluorine content of these tissues may be increased many times over the normal by excessive intakes of fluorine (3, 43, 55).

But the human subject cannot be used to assess quantitatively the disposition of absorbed fluorine in the animal body. Resort must be had to the laboratory animal and the carcass analysis technic. In a series of studies on the growing albino rat, Lawrenz and associates (18–24) obtained the following quantitative information on fluorine metabolism, working with low levels of dietary fluorine up to 13 p.p.m. of air-dried food: (a) 30 to 60 per cent of the fluorine ingested is retained in the body, and of this amount, about 95 per cent is retained in the skeleton and the remainder is about equally divided between teeth and soft tissues; (b) fluorides ingested in water solution are retained in the body to an extent some 20 per cent greater than fluorides ingested in food, when water and food ingestion are separated in time; (c) at these low levels of intake aqueous solubility does not determine the extent of fluorine absorption; (d) the intermittent feeding of fluorides induces a less complete retention in the body than does continuous feeding; (e) the growing animal adapts itself to a constant intake of fluorine by excreting larger and larger proportions and retaining less and less; (f) inadequate levels of dietary calcium, but not of dietary phosphorus, enhance the retention of dietary fluorine; (g) the concentration of fluorine in the bones responds to an increased fluorine intake to a greater degree than does the concentration of fluorine in the teeth; (h) the fluorine content of the soft tissues is also correlated with that of the diet.

Besides excretion through the kidneys and the intestinal tract, fluorine is excreted from the body in the sweat (30). The salivary glands secrete fluorine from the blood (53), and the oviduct of the hen may transfer to the egg considerable quantities of fluorine from rations containing rock phosphate (46). The placenta is permeable to the fluoride ion (16, 41), although the mammary gland is not, whether fluorine is consumed in the food (46) or in the water (51) even at high levels.

### PHYSIOLOGICAL EFFECT OF LOW LEVELS OF DIETARY FLUORINE

Although on low levels of dietary fluorine the teeth do not acquire as high a concentration of fluorine as the bones, the first signs of fluorine toxicity appear in the teeth. Also, the only established beneficial effect of fluorine relates to these organs. For a history of the investigations leading to these discoveries and for discussion of etiology and symptomatology, the reader is referred to a recent monograph edited by Dean and Kitchin (8).

Endemic dental fluorosis, or mottled enamel, in the human is generally, though not always, caused by the consumption of water containing more than 1 p.p.m. of fluorine during the period of tooth formation. If not caused by fluoriniferous water, it is caused by the consumption of foods, such as sea foods, containing considerable fluorine, as in Tristan de Cunha. Among farm animals, it may be caused by water-borne fluorine or by the use as a mineral supplement of natural phosphates containing considerable amounts of fluorine, possibly 0.3 per cent or more. It is characterized by hypoplasia of the enamel accompanied by the appearance of white opaque areas and later by brown patches. Histological changes occur in the tooth; it becomes brittle and even misshapen, and its fluorine content increases. Dean has established a remarkable correlation between the fluorine content of the communal water supply and the index of dental fluorosis associated with the continued use of such water.

The beneficial effect of low concentrations of fluorine in the domestic water supply relates to the prevention of dental caries, or tooth decay. This effect of the continued use of water containing 1 to 2 p.p.m. of fluorine has been established firmly by epidemiological and experimental studies. The use of such water, or other fluorine carrier, is the only known prophylactic treatment against this widely prevalent dental disease. Whether the effect is brought about by structural changes within the tooth, induced by absorption of fluorine by the tooth substance, or by the bacteriostatic effect of this acquired fluorine, or by changes in the buccal environment, is not known. Probably many factors are operating (6).

### TOXICITY OF EXCESSIVE INTAKES OF FLUORINE

The symptoms of chronic and acute fluorosis in man and the lower animals was comprehensively reviewed by Roholm (48) and later by Greenwood (13). Peirce (44) has published a review of chronic fluorine intoxication in domestic animals. The fluorine hazard in livestock feeding has been briefly discussed in two publications from the Committee on Animal Nutrition of the National

Research Council (38, 39). These publications give detailed descriptions and interpretations of fluorosis in animals.

In humans, chronic fluorosis is generally caused by ingestion or inhalation of fluorine-containing gases and dust; in animals, more generally by the ingestion of fluorine-bearing phosphatic supplements to low-phosphorus rations. The avidity of the bones and teeth for fluorine acts as a protection for the soft tissues possessing functions of more importance to the maintenance of life. As Peirce (44) has said: "The long latent period, a year or more in herbivora, during which the animal suffers no apparent untoward effects while steadily ingesting each day an amount of fluorine which eventually proves seriously toxic, may no doubt be explained by a gradual saturation of the skeleton until a stage is reached when its buffering effect is no longer capable of immobilizing the greater part of the absorbed fluorine, which is then free to exert general toxic effects."

During this buffering period the skeleton itself does not escape injury. Bone deformities and exostoses of various types are produced, even though not demonstrable by x-ray examination (17). Calcification of the ligaments, tendons, and fasciae contribute to the crippling effect of excessive intakes of fluorine. When the buffering action of the skeleton is no longer effective in protecting the more vital organs, degenerative changes are induced in the kidneys, liver, adrenal glands, heart, central nervous system, and finally the reproductive organs.

It is interesting to note that fluorine depresses the utilization of phosphorus in mineral phosphates by the animal as (10) well as by the plant.

From a critical study of evidence obtained with farm animals and laboratory animals (38), it would seem that a concentration of fluorine in the total ration of animals, borderline between safe and unsafe, is 100 p.p.m. on the dry basis, or somewhat less. For chickens, the level between safe and unsafe concentrations is definitely higher. For man, except for the occurrence of mottled enamel on the teeth, a urinary output of 10 to 20 mgm. of fluorine daily over many years (30) seems consistent with general good health. This would be equivalent to 50 to 100 p.p.m. of dry food. Safety would demand a selection of the lower limit in this range.

It may be said in conclusion that fluorosis in man and animals is caused by fluoriniferous waters, by foods contaminated with fluoriniferous soil, or by the inhalation or ingestion of industrial fluoriniferous wastes. The plant, except as it may carry adventitious fluorine deposits on its surfaces, cannot be incriminated in the etiology of fluorosis.

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# IRON IN LEAVES

## J. P. BENNETT

*University of California*

Most investigations on iron in plants have dealt with iron deficiency as exhibited in chlorosis. The most common cause of iron chlorosis is an excess of lime in the soil, which on account of the resulting mild alkalinity makes iron less available but does not directly injure the plant. The problem of iron availability cannot be discussed in this short paper. Attention will be limited to leaf iron, which has received much attention because it is in the leaves that the immediate effects of deficiency are seen.

Since analyses of leaves were first begun in attempts to get at the causes of chlorosis, it has been frequently reported that chlorotic leaves contain as much iron as green leaves grown under the same conditions. This has led to a belief that chlorosis is due to inactivation of iron in the leaf. Because of the strong precipitating action on iron of increasing hydroxyl-ion concentrations, increased pH of leaf tissues induced by alkaline soil might be expected to play a large part in inactivation of iron. But although saps from chlorotic tissues from plants on calcareous soil or alkaline culture solutions are occasionally found to have a higher pH value than that from green tissues, there are many cases of iron chlorosis in which chlorotic and green tissues have the same apparent pH. Several other suggestions have been offered to explain chlorosis as due to inactivation of iron, based mainly on excesses of other elements in chlorotic leaves. Inactivation has been ascribed to excess of phosphorus (7), of potassium (5), and of manganese (10).

## PHOSPHORUS IN CHLOROTIC LEAVES

The phosphorus content of chlorotic leaves is usually higher than that of green leaves from plants on calcareous soils, the excess in the former sometimes reaching 100 per cent on a fresh-weight basis. In chlorotic leaves from solution-cultured plants the excess may be even higher. Absorption of excess phosphate has been demonstrated to cause precipitation of iron along the veins of certain plants grown in solution (7), with resulting chlorosis. From this observation it has been assumed that too much phosphorus might cause inactivation of iron in any leaf. Though this may be true if a sufficient excess of phosphate reaches the leaves, the question remains whether the amounts found in leaves in lime-induced chlorosis, or that produced in alkaline culture solutions, is enough to, or does, inactivate iron to the extent of causing deficiency. In table 1 are shown the phosphorus contents of leaves of French prune trees grown in culture solution and in calcareous and noncalcareous soils. The paired culture solutions varied in the amounts of calcium, magnesium, and potassium present, and one of each pair was maintained at pH 5 to 6, the other at pH 7 to 8. Equal amounts of iron were added twice weekly to each solution. Solutions were replaced monthly.

When chlorosis appeared in the second season, leaf samples from spurs were collected near the end of May. Samples were also gathered from orchard trees. None of the trees were sprayed. Leaves were washed with distilled water. The data show that the iron found varied from 0.002 to 0.010 per cent of fresh weight, was generally higher in leaves from solution than in those from soil, and was usually about the same in leaves from each pair of acid and alkaline solutions. In all pairs, the phosphorus was higher in leaves from the alkaline solutions, and was still higher in those from soil. In three green trees, one from solution and two from soil, the phosphorus was as high as or higher than in several of the chlorotic trees. It may be concluded from these results that the excess of phosphorus found in leaves of trees under ordinary conditions of solution or soil culture does not, at least directly, cause chlorosis by precipitating iron. Furthermore, attempts to produce chlorosis by injecting phosphate solution into tree branches previous to leaf development failed, although the phosphorus content of leaves was increased many fold.

### POTASSIUM IN CHLOROTIC LEAVES

Potassium accumulates in chlorotic leaves in excess (11) that may reach 100 per cent of that in green leaves from soil or solution culture. In table 1 are shown potassium contents of leaves of the same trees discussed in the preceding section. Potassium was always higher in leaves from the alkaline solution of each pair, and was as high or higher in leaves from alkaline soil in comparison with the noncalcareous soil. In two of the green trees potassium was as high as, or higher than, it was in six of the chlorotic trees. The higher potassium content of chlorotic leaves is frequently accompanied by lowered calcium content (5, 11). But whether the calcium content is higher or lower, the large excess of potassium results in an increased potassium-calcium ratio in chlorotic leaves. In table 1 it may be seen that these ratios were always higher in leaves from alkaline solutions or soil, and were lower in leaves from soil than in most of those from solution. But ratios were higher in some green than in some chlorotic leaves.

Potassium deficiency causes a chlorosis of plum trees (12) that resembles lime-induced chlorosis and appears to be the result of a disturbance in the functioning of iron. The chlorotic leaves do not respond to iron applications which usually cure lime-induced chlorosis, but they do become green if large applications are made. In this form of chlorosis potassium is lower and calcium higher, and potassium-calcium ratios are lower in chlorotic than in green leaves. A disturbed iron function thus is caused in this case by a relation of potassium to calcium opposite to that existing in lime-induced chlorosis. It does not seem probable, therefore, as has been suggested (5), that chlorosis is caused by a disturbed potassium-calcium balance or by displacement of iron from a chlorophyll-producing enzyme by an excess of potassium.

In the experiments presented in table 1 alkaline culture solutions usually produced chlorotic and acid solutions green leaves. But in the solution with high potassium plus high calcium both trees were green, whereas in the solution with potassium, calcium, and magnesium all at the high level, both were chlorotic.

## TABLE 1

Iron, phosphorus, potassium, and calcium content, as percentage of fresh weight, and ratios of potassium to calcium in leaves of French prune grown in soil and in solutions with different levels of potassium, calcium, and magnesium

| | HIGH*-Ca SOLUTION | | HIGH-Mg SOLUTION | | HIGH-K SOLUTION | | HIGH-CaK SOLUTION | | HIGH-MgK SOLUTION | | HIGH-CaMg SOLUTION | | HIGH-CaMgK SOLUTION | | SOIL CALCAREOUS | | NON-CALCAREOUS SOIL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 5-6 | 7-8 | 5-6 | 7-8 | 5-6 | 7-8 | 5-6 | 7-8 | 5-6 | 7-8 | 5-6 | 7-8 | 5-6 | 7-8 | 8 | 8 | 6 |
| Leaves | G† | C† | G | C | G | C | G | G | G | C | G | C | C | C | G | C | G |
| **Leaf analysis** | | | | | | | | | | | | | | | | | |
| Fe | 0.010 | 0.009 | 0.005 | 0.005 | 0.007 | 0.003 | 0.005 | 0.004 | 0.006 | 0.007 | 0.008 | 0.008 | 0.009 | 0.010 | 0.002 | 0.002 | 0.004 |
| P | 0.036 | 0.066 | 0.036 | 0.062 | 0.037 | 0.047 | 0.037 | 0.046 | 0.034 | 0.060 | 0.034 | 0.058 | 0.035 | 0.049 | 0.082 | 0.088 | 0.091 |
| K | 0.34 | 0.65 | 0.39 | 0.66 | 0.80 | 1.01 | 0.61 | 0.88 | 0.66 | 0.88 | 0.27 | 0.50 | 0.72 | 0.91 | 0.39 | 0.47 | 0.40 |
| Ca | 0.34 | 0.29 | 0.25 | 0.18 | 0.26 | 0.27 | 0.23 | 0.30 | 0.21 | 0.19 | 0.29 | 0.26 | 0.18 | 0.22 | 0.57 | 0.39 | 0.70 |
| K/Ca | 1.0 | 2.2 | 1.6 | 3.7 | 3.1 | 3.7 | 2.7 | 2.9 | 3.1 | 4.2 | 0.9 | 1.9 | 4.0 | 4.1 | 0.7 | 1.2 | 0.6 |

* High = 4 times normal.

† G = green, C = chlorotic.

Two of the trees in soil were green and one chlorotic. The statements made concerning amounts of both potassium and phosphorus and the ratio of potassium to calcium apply also to these three groups considered apart from the remainder of the series. Though it is evident that nutritional conditions may affect chlorosis, it is not possible to deduce the probability of its appearance or point to its cause either from absolute amounts of potassium or phosphorus found or from the ratio of potassium to calcium.

## MANGANESE IN CHLOROTIC LEAVES

Manganese-induced chlorosis resembles lime-induced chlorosis in being cured by iron application. It has been suggested that manganese inactivates iron in leaves by oxidizing it to the ferric state with consequent precipitation as ferric organic complexes (10). In table 2 are shown the results of growing tomato plants in culture solutions at pH 5.5 to 6 with manganese supplied as manganous sulfate and iron as ferrous sulfate.[1] The data (part A) show that increasing manganese in the solution with iron uniform resulted in increasing amounts of the former in the leaves and decreasing amounts of the latter and of chlorophyll. Chlorosis appeared when the iron decreased to about 105 p.p.m. and chlorophyll to 1.3 per cent of the dry weight. The ratio of manganese to iron ranged from 4 to 47 in green, and from 60 to 108 in chlorotic leaves. With manganese uniform and iron increased in the solution (part B) manganese decreased and iron and chlorophyll increased in the leaves. Chlorosis appeared when the iron was about 115 p.p.m. and the chlorophyll 1.3 per cent of the dry weight. The ratio of manganese to iron ranged from 17 to 27 in green and from 36 to 64 in chlorotic leaves. The manganese ranged from 580 to 5,100 p.p.m. in green leaves, and in chlorotic leaves from 4,160 to 10,000 p.p.m. of the dry weight.

It seems clear from these data that, for tomato at least, manganese is not very toxic, that it does not interfere with utilization of iron in the leaf, and that the ratio of manganese to iron in the tissue has no relation to the chlorosis produced. Manganese evidently produced chlorosis by depressing absorption of iron, an antagonism existing between the two elements which is apparently mutual. It is possible that upward transport of iron is hindered by excess of manganese, but if so, it does not affect the conclusions drawn from the data. Only analyses of upper leaves are shown in table 2. Lower leaves in the series shown in part A were all green; those shown in part B were the same as the upper leaves. Analyses of lower leaves agreed with those of upper leaves in the relation of iron to chlorophyll, but manganese concentration was higher and manganese-iron ratios were higher, reaching a value of 127 in one set of green leaves.

## SURFACE CONTAMINATION OF LEAVES

In the data of tables 1 and 2 there is a possible defect in that the leaves were washed only with distilled water. Recent work (2) has shown that surface

[1] Kriel, H. T. A study of the effect of excess manganese on iron and chlorophyll content and growth of tomato plants. 1941. [Unpublished thesis. Copy on file University of California, Berkeley.]

## TABLE 2

Manganese and iron content of leaves of tomato grown in culture solution with nearly constant iron and varied manganese supply (A), and with nearly constant manganese and varied iron supply (B)

| **A** Mn IN CULTURE SOLUTION.....p.p.m. | 5 | 20 | 40 | 80 | 100 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|---|
| Fe IN CULTURE SOLUTION.....p.p.m. | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| **Leaf analysis** | | | | | | | | |
| Condition................. | Green | Green | Green | Green | Chlorotic | Chlorotic | Chlorotic | Chlorotic |
| Fresh weight..........gm. | 246 | 204 | 153 | 98 | 72 | 73 | 38 | 12 |
| Mn, dry weight.....p.p.m. | 580 | 1,800 | 2,820 | 4,930 | 6,600 | 9,000 | 8,100 | 10,000 |
| Fe, dry weight.....p.p.m. | 133 | 122 | 110 | 106 | 107 | 105 | 94 | 93 |
| Chlorophyll, dry weight.....per cent | 2.00 | 1.70 | 1.66 | 1.36 | 1.29 | 1.15 | 1.08 | |
| Mn/Fe..................... | 4 | 15 | 26 | 47 | 62 | 60 | 85 | 108 |

| **B** Mn IN CULTURE SOLUTION.....p.p.m. | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
|---|---|---|---|---|---|---|---|---|
| Fe IN CULTURE SOLUTION.....p.p.m. | 50 | 25 | 12.5 | 8 | 5 | 2 | 1 | 0.5 |
| **Leaf analysis** | | | | | | | | |
| Condition................. | Green | Green | Green | Green | Green | Chlorotic | Chlorotic | Chlorotic |
| Fresh weight..........gm. | 35 | 102 | 127 | 160 | 137 | 108 | 14 | 1.6 |
| Mn, dry weight.....p.p.m. | 5,100 | 3,520 | 3,400 | 3,400 | 3,440 | 4,160 | 4,360 | 6,200 |
| Fe, dry weight.....p.p.m. | 250 | 200 | 168 | 150 | 125 | 115 | 98 | 97 |
| Chlorophyll, dry weight.....per cent | 2.12 | 1.95 | 1.63 | 1.66 | 1.70 | 1.32 | 0.82 | 0.66 |
| Mn/Fe..................... | 22 | 17 | 20 | 23 | 27 | 36 | 45 | 64 |

contamination may cause large error in iron determination. Leaves from the field, especially if they have been heavily sprayed with lime-containing materials, may carry iron as surface contamination amounting to several times that in the tissue. Unsprayed field leaves may also carry much iron-containing dust. It is less but not absent in greenhouse-grown material. It is usually less, the younger the leaves. Washing with distilled water does not effectively remove surface contamination, especially from leaves sprayed with lime-containing materials. The contamination left on such leaves after careful washing with water may cause error up to 300 per cent in iron determinations. Complete removal of surface contamination from leaves bearing lime-containing sprays requires rubbing the leaf surface while submerged in dilute acid, and subsequent rinsing. It may be removed from unsprayed leaves by washing with dilute acid or an iron-free detergent.

Since much of the material that has been analyzed for iron has been collected from the field and commonly late in the season, and investigators often do not mention washing or, if so, only washing with distilled water, many of the available data on iron are open to doubt. In the experiments reported in table 2 the plants were grown in a greenhouse and the leaves were young, and therefore probability of accumulating much dust was small. The leaves were washed in distilled water. As the iron analyses were consistent, it is improbable that contamination was large. The prune trees of table 1 were grown outdoors under coastal city conditions, except for the soil-grown trees, which were from orchards. All the leaves were unsprayed and were about 6 weeks old when collected. The surface contamination was therefore probably not great. The iron values were not unusually high or irregular. Contamination may, however, have been present in significant amount and makes calculation of ratios of phosphorus and potassium to iron untrustworthy, since the iron content given may have been too high. But this does not affect the statements or conclusions based on the absolute amounts of phosphorus, potassium, or calcium, or the ratio of potassium to calcium, these substances being present in such large amounts as to be little influenced by surface contaminants.

### SAMPLING AND CALCULATION

The iron content of leaves varies with species, leaf age, and soil conditions. It increases rapidly during growth of leaves, then slowly after full size is reached, until the end of the season. Leaves of plants on noncalcareous soil contain more iron than those of plants on calcareous soil. The iron content of leaves of plants grown in solutions is strongly influenced by the rate of iron feeding. Iron is usually lower in rapidly growing than in slowly growing shoots. These are reflections of the availability of iron in soil or solution and of the plants' ability to get the iron from the soil or solution, as well as of the rate of growth.

Leaf samples for study of chlorosis are necessarily chosen visually. No standardization has been devised whereby one can be assured of selecting fully comparable samples at different times or at the same time from different plants. Visual selection aims at obtaining leaves of comparable chlorophyll content,

but is complicated by variable distribution of the chlorophyll present, by the earlier fall of chlorotic leaves, and by the difficulty of judging leaves of different species. Some standardized method of selection is needed wherever analytical data are to be compared on the basis of color variation.

Iron content is usually calculated on the dry weight of tissue, which distorts the results because of differences in percentage dry weight of leaves of different species, of chlorotic and green leaves, and of those of different age. Calculation on fresh weight reduces the effect of variable dry weight but is objectionable

## TABLE 3

*Total iron and chlorophyll content, as percentage of fresh, dry, and protein weight, of leaves of the same approximate age of three species of plants*

| CONDITION OF LEAVES | PEAR (PER CENT DRY WEIGHT = 22 TO 30) | | | CORN (PER CENT DRY WEIGHT = 14 TO 16) | | | TOBACCO (PER CENT DRY WEIGHT = 7.6 TO 8.7) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fresh weight | Dry weight | Protein weight | Fresh weight | Dry weight | Protein weight | Fresh weight | Dry weight | Protein weight |
| **Chlorotic** | | | | | | | | | |
| Severely | | | | | | | | | |
| Fe...................... | 0.0004 | 0.0019 | 0.0101 | 0.0003 | 0.0024 | 0.0204 | 0.0006 | 0.0079 | 0.0316 |
| Chlorophyll............. | 0.038 | 0.17 | 0.95 | 0.035 | 0.25 | 2.12 | 0.018 | 0.24 | 0.96 |
| Moderately | | | | | | | | | |
| Fe...................... | 0.0006 | 0.0027 | 0.0134 | 0.0004 | 0.0031 | 0.0228 | 0.0006 | 0.0087 | 0.0382 |
| Chlorophyll............. | 0.060 | 0.25 | 1.24 | 0.078 | 0.54 | 3.96 | 0.037 | 0.51 | 2.24 |
| Slightly | | | | | | | | | |
| Fe...................... | 0.0006 | 0.0024 | 0.0128 | | | | | | |
| Chlorophyll............. | 0.085 | 0.34 | 1.81 | | | | | | |
| | | | | | | | | | |
| **Green** | | | | | | | | | |
| Light | | | | | | | | | |
| Fe...................... | 0.0010 | 0.0036 | 0.0197 | 0.0006 | 0.0041 | 0.0257 | 0.0006 | 0.0070 | 0.0292 |
| Chlorophyll............. | 0.164 | 0.61 | 3.34 | 0.121 | 0.81 | 5.14 | 0.058 | 0.74 | 3.09 |
| Medium | | | | | | | | | |
| Fe...................... | 0.0011 | 0.0040 | 0.0208 | 0.0008 | 0.0056 | 0.0325 | 0.0005 | 0.0073 | 0.0250 |
| Chlorophyll............. | 0.208 | 0.74 | 3.85 | 0.176 | 1.22 | 7.08 | 0.082 | 1.11 | 3.81 |
| Dark | | | | | | | | | |
| Fe...................... | 0.0014 | 0.0047 | 0.0237 | 0.0016 | 0.0100 | 0.0566 | 0.0010 | 0.0115 | 0.0386 |
| Chlorophyll............. | 0.266 | 0.89 | 4.48 | 0.276 | 1.71 | 9.70 | 0.132 | 1.54 | 4.70 |

because fresh weight may vary from time to time and loss may occur rapidly during handling. Area has been suggested as a basis but is objectionable in that it does not take into account differences in leaf thickness or in amount occupied by walls, and changes with water content, all of which would be important in comparing different species. Calculation on the water content is objectionable in that, besides its variability, part of the water is in walls and vacuoles where there is little or perhaps no iron. The objections to calculation on a per leaf basis are readily apparent. Since iron is contained almost wholly in the proto- plasm, the obvious reference basis is the protein content of the tissue, which most

nearly represents the amount of protoplasm present and changes but slowly. The objections to it are that storage proteins are sometimes present, it must be referred to some other base to determine changes, and it requires an additional determination. In leaves where little storage protein is present, the total, or preferably the insoluble, nitrogen converted to protein by the conventional factor affords an approximation of the amount of living substance present. Other methods for protein estimation are, of course, available. The protein data presented later were determined by precipitation with trichloracetic acid. As no one reference basis will serve for all purposes, it seems in most cases desirable to use at least more than one.

In table 3 are presented the comparative iron and chlorophyll contents of leaves of similar age of three species of plants that vary widely in dry matter. One, pear, was grown in calcareous soil and represents a typical case of lime-induced chlorosis. The other two, corn and tobacco, were grown in culture solution, various degrees of chlorosis being produced by limiting the iron supply. On the protein basis, both iron and chlorophyll varied less from chlorotic to green leaves than when referred to either fresh or dry weight, and showed a better agreement with the sampling. Between species the effects of both water and unrelated dry matter were avoided, the data representing approximately the concentration of iron and chlorophyll in the dry matter of living protoplasm.

## IRON AND CHLOROPHYLL IN PEAR LEAVES

In lime-induced iron chlorosis leaves are chlorotic or green when they develop. Chlorotic leaves may subsequently become green with favorable iron supply from soil or by application, but leaves once green remain so. Since iron content increases with age, comparison over a season is best made on leaves from spurs which are all approximately the same age. In table 4 is presented such a seasonal study of iron and chlorophyll content of adequately washed pear leaves calculated on fresh, dry, and protein weight basis.

The data show that iron was much lower in chlorotic than in green leaves, especially early in the season. Accumulation took place in all leaves during the whole season, from one third to one half occurring before late April (see table 3), the remainder during the long period from April until late September. This is clearly evident only on the protein basis. About one fifth of the apparent increase during the latter period was due to decrease of protein. The increase was somewhat greater in chlorotic than in green leaves. As a result, the ratios of iron in the most chlorotic to that in the greenest leaves on the protein basis were in the four sets, in order of collections, 0.4, 0.7, 0.8, and 0.9, while at the same time the ratios of chlorophyll showed little or no change. It is evident, on the protein basis, that had the amount of iron in chlorotic leaves in late season been present in early season, the leaves would doubtless have been green. This is not evident on the dry basis and appears doubtful on the fresh basis.

About half the total chlorophyll finally present was formed before the first collection in April (see table 4), the remainder over the period from April to September. As with iron, about one fifth the apparent increase was accounted

for by decrease of protein. There was thus a real increase of both iron and chlorophyll during the whole season, the larger part of iron accumulation occurring after April, and of chlorophyll, before. It is apparent that iron entering the leaf very early in the season is much more effective for chlorophyll formation than that entering later. This agrees with experience in applying iron to chlorotic leaves by spray or injection. Application in April resulted in full greening in a week, in 2 weeks in May, in 4 weeks in July, whereas later applications produced very slow or no apparent greening. It seems clear that chlorosis

TABLE 4

*Total iron and chlorophyll content, as percentage of fresh, dry, and protein weight, of spur leaves of pear**

| CONDITION OF LEAVES | JUNE 3 (PER CENT DRY WEIGHT = 30 TO 37) | | | JULY 21 (PER CENT DRY WEIGHT = 30 TO 40) | | | SEPTEMBER 22 (PER CENT DRY WEIGHT = 38 TO 43) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fresh weight | Dry weight | Protein weight | Fresh weight | Dry weight | Protein weight | Fresh weight | Dry weight | Protein weight |
| **Chlorotic** | | | | | | | | | |
| Severely | | | | | | | | | |
| Fe..................... | 0.0007 | 0.0021 | 0.0187 | 0.0007 | 0.0022 | 0.0236 | | | |
| Chlorophyll............ | 0.038 | 0.13 | 1.16 | 0.027 | 0.09 | 0.97 | | | |
| Moderately | | | | | | | | | |
| Fe..................... | 0.0008 | 0.0022 | 0.0182 | 0.0009 | 0.0026 | 0.0249 | 0.0012 | 0.0032 | 0.0376 |
| Chlorophyll............ | 0.074 | 0.21 | 1.74 | 0.059 | 0.17 | 1.63 | 0.099 | 0.26 | 3.06 |
| Slightly | | | | | | | | | |
| Fe..................... | 0.0008 | 0.0023 | 0.0206 | 0.0011 | 0.0030 | 0.0279 | 0.0014 | 0.0033 | 0.0374 |
| Chlorophyll............ | 0.121 | 0.34 | 3.05 | 0.097 | 0.26 | 2.41 | 0.156 | 0.37 | 4.20 |
| **Green** | | | | | | | | | |
| Light | | | | | | | | | |
| Fe..................... | | | | 0.0012 | 0.0029 | 0.0270 | 0.0015 | 0.0036 | 0.0398 |
| Chlorophyll............ | | | | 0.208 | 0.52 | 4.85 | 0.195 | 0.46 | 5.08 |
| Medium | | | | | | | | | |
| Fe..................... | 0.0010 | 0.0028 | 0.0220 | 0.0014 | 0.0037 | 0.0303 | 0.0017 | 0.0039 | 0.0414 |
| Chlorophyll............ | 0.240 | 0.65 | 5.10 | 0.270 | 0.69 | 5.65 | 0.249 | 0.58 | 6.03 |
| Dark | | | | | | | | | |
| Fe..................... | 0.0014 | 0.0039 | 0.0255 | 0.0017 | 0.0046 | 0.0305 | 0.0019 | 0.0047 | 0.0425 |
| Chlorophyll............ | 0.346 | 0.94 | 6.13 | 0.293 | 0.78 | 5.20 | 0.332 | 0.82 | 7.42 |

* For April 28 figures, see table 3.

was in this case the result of low iron supply in the early part of the season. And since the leaves developed in the chlorotic condition, the earlier they were collected the more indicative were the analyses.

#### ACTIVE AND RESIDUAL IRON

It is readily apparent from the data in table 4 that most of the iron in chlorotic leaves was ineffective for chlorophyll promotion. And it is also evident that much of that entering green leaves, especially after April, was likewise ineffective. The trend of concentrations of iron and chlorophyll in passing from green to

chlorotic leaves indicates that at the zero chlorophyll level there would be still considerable iron present in the leaves at any season. If it is assumed that the ineffective iron fraction remained the same or changed at a constant rate from green to chlorotic leaves of a single collection, it can be shown by plotting iron against chlorophyll that the additional iron above that in chlorophyll-free leaves was proportional to chlorophyll. The iron of leaves has in this way been placed in two categories, one proportional to chlorophyll, called "active" iron, the other with no apparent direct relation to chlorophyll, called "inactive" iron (8). The term "inactive" is unsatisfactory because the iron so described may be considered indirectly related to chlorophyll production through its part in the building of the cell and especially the chloroplast, and is no doubt active in other ways Instead of "inactive" the term "residual" will be applied to this fraction of iron.

The first estimations of active iron were made by extracting leaf material with dilute HCl (8). The residual fraction was found to be decidedly variable. This was probably due to surface contamination, since the total iron was likewise variable. Later estimations on adequately washed leaves showed that both acid-soluble and total iron had the same relation to active iron (2). Application of the same method to isolated chloroplasts from chlorotic and green leaves showed that they contained both active and residual iron, and that all the active and much of the residual iron of the cell was in the chloroplasts (2). Localization of active iron in the chloroplast was to be expected, as the chloroplast is the seat of chlorophyll formation. These observations agree with the determined distribution of total iron in cells. In green spinach leaves up to 82 per cent (4), in green tobacco leaves 61 to 81 per cent, and in chlorotic tobacco leaves 43 to 71 per cent of the total iron have been found in the chloroplasts (2).

In table 5 are shown estimations of active iron made from the data of table 4 on the protein basis. Residual iron was constant in a single collection but increased throughout the season. Only one fourth to one fifth of the final amount was present in the April collection. About one fifth of the apparent increase between April and September was due to seasonal decrease of protein. Active iron was high in all leaves in April, but it formed only 32 per cent of total iron in the most chlorotic leaves whereas in the greenest leaves it formed 72 per cent. By June, active iron had decreased to about one half its level in April, where it stayed during the remainder of the season, but remained always higher, the greener the leaf. In early season a variable but relatively large fraction of entering iron went into the form of active iron, but most of that entering later went into the residual fraction. Some of the active iron present early apparently also passed later into the residual fraction. This does not appear impossible, since the active fraction is easily removed from the chloroplast, in contrast with the residual iron, which dissolves slowly in dilute HCl. Distribution of incoming iron between the two fractions seems to be related to rate of entry and to relative capacity of the substances with which it becomes associated to absorb and retain it. Active iron was built up quickly but not strongly held, whereas residual iron accumulated slowly and was strongly bound. Once iron has entered the residual state it apparently cannot be utilized for chlorophyll production.

From 40 to 60 per cent of the final amount of chlorophyll was also present in April, except in the most chlorotic leaves, where there was no seasonal increase. The rate of production was high in the early season, in agreement with high active iron at that time. On a time basis, production was about twice as rapid per unit of active iron in early season as later. The ratio of active iron to chlorophyll was,

TABLE 5

*Active and residual iron and chlorophyll, on the protein weight basis, in spur leaves of pear*

| CONDITION OF LEAVES | APRIL 28 | | | JUNE 3 | | | JULY 21 | | | SEPTEMBER 22 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Iron | | Chloro-phyll | Iron | | Chloro-phyll | Iron | | Chloro-phyll | Iron | | Chloro-phyll |
| | Re-sidual | Active | | Re-sidual | Active | | Re-sidual | Active | | Re-sidual | Active | |
| | *p.p.m.* | *p.p.m.* | *per cent* | *p.p.m.* | *p.p.m.* | *per cent* | *p.p.m.* | *p.p.m.* | *per cent* | *p.p.m.* | *p.p.m.* | *per cent* |
| Chlorotic | | | | | | | | | | | | |
| Severely | 69 | 32 | 0.95 | 175 | 12 | 1.16 | 227 | 9 | 0.97 | | | |
| Moderately | 87 | 47 | 1.24 | 162 | 20 | 1.74 | 231 | 16 | 1.63 | 362 | 24 | 3.06 |
| Slightly | 64 | 64 | 1.81 | 174 | 32 | 3.05 | 252 | 24 | 2.41 | 342 | 36 | 4.20 |
| Green | | | | | | | | | | | | |
| Light | 81 | 116 | 3.34 | | | | 230 | 48 | 4.85 | 358 | 46 | 5.08 |
| Medium | 68 | 140 | 3.85 | 150 | 70 | 5.10 | 231 | 63 | 5.65 | 364 | 58 | 6.03 |
| Dark | 66 | 168 | 4.48 | 168 | 87 | 6.02 | 230 | 66 | 5.20 | 353 | 72 | 7.42 |
| Residual iron, av.......... | 73 | | | 166 | | | 234 | | | 356 | | |
| $\dfrac{\text{Chlorophyll}}{\text{Active iron}}$ .. | | | 276 | | | 772 | | | 916 | | | 1,092 |

of course, the same in all leaves in a collection, but decreased during the season, as a result both of increased chlorophyll and of decreased active iron.

### NITROGEN AND CHLOROPHYLL

Disturbance of nitrogen distribution has often been found associated with chlorophyll deficiency. Leaves of albino shoots and the yellow or white regions of variegated leaves contain more soluble and less insoluble nitrogen than do corresponding green tissues. In many cases of nutritional disturbance, including iron chlorosis, or of disease caused by virus or organisms, where chlorophyll deficiency results, a similar situation has been found. In severely chlorotic leaves of pears as much as 25 per cent of the leaf nitrogen was found in soluble form in comparison with 5 per cent in green leaves, with total nitrogen about the same in both. Applications of iron to chlorotic leaves resulted in both greening and reduction of the soluble nitrogen, accompanied by increase of the insoluble nitrogen, to normal levels. Evidently chlorotic leaves are unable to convert all of their soluble nitrogen to protein. This has been ascribed to lack of carbohydrates, but the explanation apparently cannot be true because chlorotic and green leaves contain the same amount of sugar, and chlorotic leaves develop

on stored carbohydrates, which indicates that they can utilize such forms. The failure appears to be directly due to deficiency of iron.

If the data on nitrogen distribution and chlorophyll content of the pear leaves used for tables 4 and 5 are arranged so that chlorophyll can be plotted against protein, it can be shown that the increase in chlorophyll was proportional to the increase in protein. The increase of protein thus showed the same relation to total protein as did active iron to total iron, and may be referred to as "active

### TABLE 6

*Soluble nitrogen, total, active, and residual protein,\* and chlorophyll, as percentage of fresh weight, in spur leaves of pear*

| CONDITION OF LEAVES | APRIL 28 | | | JUNE 3 | | | JULY 21 | | | SEPTEMBER 22 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Soluble N | Protein total (Active) | Chlorophyll | Soluble N | Protein total (Active) | Chlorophyll | Soluble N | Protein total (Active) | Chlorophyll | Soluble N | Protein total (Active) | Chlorophyll |
| **Chlorotic** | | | | | | | | | | | | |
| Severely | 0.36 | 4.2 (0.3) | 0.038 | 0.15 | 3.5 (0.3) | 0.039 | 0.14 | 2.8 (−0.1) | 0.027 | | | |
| Moderately | 0.28 | 4.8 (0.9) | 0.059 | 0.11 | 4.2 (1.0) | 0.074 | 0.13 | 3.6 (0.7) | 0.059 | 0.11 | 3.2 (0.9) | 0.099 |
| Slightly | 0.19 | 4.6 (0.7) | 0.085 | 0.09 | 3.9 (0.7) | 0.121 | 0.15 | 4.0 (1.1) | 0.097 | 0.11 | 3.6 (1.3) | 0.156 |
| **Green** | | | | | | | | | | | | |
| Light | 0.09 | 5.0 (1.1) | 0.170 | | | | 0.11 | 4.3 (1.4) | 0.208 | 0.12 | 3.9 (1.6) | 0.195 |
| Medium | 0.12 | 5.5 (1.6) | 0.208 | 0.06 | 4.7 (1.5) | 0.240 | 0.15 | 4.7 (1.8) | 0.270 | 0.12 | 4.0 (1.7) | 0.249 |
| Dark | 0.09 | 5.9 (2.0) | 0.266 | 0.04 | 5.6 (2.4) | 0.344 | 0.12 | 5.6 (2.7) | 0.293 | 0.07 | 4.6 (2.3) | 0.332 |
| Residual protein | | 3.9 | | | 3.2 | | | 2.9 | | | 2.3 | |
| Chlorophyll / Active protein | | | 0.125 | | | 0.135 | | | 0.126 | | | 0.132 |

\* Protein = protein N $\times$ 5.7.

protein," the term "active" meaning that it is closely associated with the chlorophyll production. The remainder of the protein corresponds to residual iron and may be called "residual protein." The estimations of active and residual protein are shown in table 6.

Since both active iron and active protein were proportional to chlorophyll, they were proportional to each other. Because of this it appears logical to assume that active iron was associated with active protein, and residual iron with residual protein. Protein is the most abundant substance in the protoplasm and is known to have considerable binding capacity for iron (9). On this basis the data of tables 5 and 6 indicate that the total iron was distributed between

the active and residual fractions of protein, and that the distribution varied between chlorotic and green leaves and at different times of the season. Thus in April in the most chlorotic leaves one third of the iron was active and was in the relatively small active protein fraction, whereas in the greenest leaves nearly three fourths of it was active and was in the relatively large active protein fraction.

The remainder, constant in amount, was in the residual protein. At this time iron was about five times as concentrated in the active as in the residual protein. By June it was about one and one half, and in September about five times as concentrated in residual as in active protein. Most of this shift came about as the result of steady seasonal increase in residual iron, but part was due to decrease of active iron.

Though nothing is known of the nature of the proteins in pear leaves, evidence has been obtained in the chloroplasts of spinach leaves (4) that the residual iron is associated with phosphoproteins which have considerable capacity to bind iron (9). What may be the nature of the active protein fraction is unknown, but it is evident that it binds iron less strongly than the residual protein. The development of chlorophyll appears to depend on a sufficiently rapid rate of entry of iron that not all of it is absorbed by the residual protein. The excess above that so absorbed determines the degree of chlorosis or greenness.

Whether or not the foregoing discussion is a correct interpretation of the data, it seems clear that chlorosis is a disturbance of nitrogen metabolism as well as of iron metabolism and that the two are intimately related. The influence of various nutritional factors would probably be exerted through their relation to nitrogen metabolism, particularly any effect they might have on the nature and amount of the proteins produced.

The possibility of an association of chlorophyll and protein in a complex (6) has received considerable attention since it was first suggested. The composition of such a complex prepared from leaf suspension or from isolated chloroplasts as reported varied from 5.5 to 27 parts of chlorophyll to 100 parts of protein. In chloroplasts from chlorotic and green leaves of corn 9 to 18 parts, and in tobacco 6 to 20 parts, of chlorophyll per 100 parts of chlorophyll were found. In view of the data in tables 5 and 6 it seems evident that residual as well as active protein was included in the amounts determined. If a chlorophyll-protein complex exists it seems probable that it would consist of active protein and chlorophyll. It also seems probable that it might be uniform in composition in a single species, and vary among species. In table 6 the ratio of chlorophyll to active protein in the four collections of pear leaves ranged from 0.125 to 0.135, averaging 0.13, or 13 parts of chlorophyll per 100 parts of protein. On the same basis the ratios were such that in corn there were 22 parts, and in tobacco 30 parts of chlorophyll per 100 parts of protein. In mols of chlorophyll this would be for pear 10, for corn 17, and for tobacco 23 mols per 68,000 parts of protein.

Iron has been found associated with a reported chlorophyll-protein complex (2), but because of the manner of preparation of the complex, both residual and active iron were probably included. The proportionality between active iron

and active protein indicated in tables 5 and 6 suggests that if iron is a constituent of a chlorophyll-protein complex, thus making it an iron-chlorophyll-protein complex, it would be the active iron. If such a complex existed it was not constant in iron content during the season, since the ratios of active iron to chlorophyll, and to active protein, decreased seasonally as indicated in table 5. Such a shift in iron content does not seem impossible, as active iron is not strongly held and some of it might pass out of the complex into the residual protein. But the decrease in ratio suggests that the active iron was a catalyst rather than merely a constituent of a complex.

So far, iron has been considered without regard to its state of oxidation or solubility. Iron is generally assumed to enter and move in solution, but it is also possible that it may not only enter but be transferred within the cell by a process of exchange along or between surfaces (3); however, soluble iron is always found in plant sap, the amount varying widely in different plants. Since all plant tissues contain organic acid radicals, which are often good iron solvents, it is suspected that the soluble iron in saps, or in extracts, does not represent accurately the amount in intact cells, but largely comes into solution as a result of mixing of protoplasm with vacuolar sap during extraction. This appears to be the probable reason for the high proportion of soluble iron found in plants with the more acid saps (1). Most of the iron in cells is not in solution, little being present in vacuolar sap. The insoluble fraction includes metabolically active iron, such as iron enzymes, the active fraction associated with chlorophyll formation, and at least some of the residual iron present in chlorophyll-free tissues.

Tissue suspensions contain both ferrous and ferric iron in an easily displayed equilibrium. Extraction of an aliquot with $o$-phrenantholine yields a quantity of ferrous iron, and extraction of another aliquot with ferron yields a quantity of ferric iron, the sum of the two often exceeding the total iron known to be present. Chloroplasts of spinach (4) are reported to contain both ferrous and ferric iron. A small water-soluble fraction was all ferrous. In extracts with dilute HCl or KOH both ferrous and ferric forms were apparently present, whereas in a large remaining fraction only ferric iron was found. Distribution between ferrous and ferric states may be expected to vary in living cells with cell activity and with iron supply. It is suspected that the active iron associated directly with chlorophyll is ferrous, whereas residual iron is ferric. Distribution between these two forms is undoubtedly influenced by oxidation-reduction conditions in the cell. If this is true, the distribution of iron between active and residual forms, and between active and residual protein may depend more on its distribution between the ferrous and ferric state than on differences in the nature of active and residual protein, both of these being, however, modifiable by the living cell.

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# CERTAIN FACTORS AFFECTING THE AVAILABILITY, ABSORPTION, AND UTILIZATION OF MAGNESIUM BY PLANTS[1]

## H. P. COOPER

*South Carolina Agricultural Experiment Station*

Magnesium is one of the essential elements in the growth of plants. It is usually present in smaller amounts than calcium, and is relatively more abundant in the parts of the plants concerned with vital processes such as seeds and foliage than in such parts as stems and roots. Miller (15) points out the significance of magnesium in plant nutrition.

Most soils contain a sufficient supply of available magnesium for most of the crops commonly grown. Under certain conditions many soils may not contain sufficient magnesium for optimum growth. The deficiency areas are usually associated with relatively heavy precipitation and leaching of magnesium from the soil. The addition of considerable quantities of fresh irrigation water to soils in humid regions may result in the loss of magnesium and the occurrence of magnesium deficiency in certain crops.

There are several important physical and chemical properties of magnesium and other conditions which may be considered in determining the availability and the loss of magnesium from soils. Some of the more important factors are: (*a*) intensity of the binding of normal valence electrons as determined by standard electrode potentials and the equivalent energy required for the removal of the normal valence electrons; (*b*) the degree of solubility of magnesium compounds present in the soil complexes; (*c*) the amount of leaching occurring in the soil; (*d*) the intensity of absorption of nutrient elements by plants; (*e*) the relation of the strength of nutrient ions to the quality of light utilized in photosynthesis; and (*f*) the relation of climate, soil type, fertilizer, and liming practices.

## INTENSITY OF REMOVAL OF CATIONS FROM SOIL BY ELECTRODIALYSIS

The relative intensity of the removal of magnesium from the soil colloidal complex is of interest in considering the loss of magnesium from the soil. The relative intensity of the removal of various ions from Hyde clay loam is illustrated in table 1, showing the results from the electrodialysis of a 20-gm. composite sample composed of equal amounts of potassium-, sodium-, calcium-, and magnesium-saturated soils. The proportion of the total amount of potassium, sodium, calcium, and magnesium in the sample which was extracted during the first 2-hour period was 56.00, 24.66, 17.49, and 11.98 per cent, respectively. It is noted that the intensity of the removal of ions was in the same order as the strength of ions. With potassium, sodium, and calcium a large proportion of the ions was removed during the first two extraction periods, whereas there was no marked difference in the percentage extractions of magnesium for the first six periods.

### RELATION OF ELECTRODE POTENTIAL TO CATION EXCHANGE

The electromotive force series of elements listed by Cooper (5, 6), Collings (3), and Hodgman and Holmes (13) may be very helpful in interpreting the cation-exchange reactions occurring in soil studies. The intensity of removal from the soil of cations with the same valence is apparently related to the electrode potentials. On this basis, since magnesium has a lower standard electrode potential than potassium, sodium, or calcium, the intensity of its removal by electrodialysis would be lower than that of metals higher in the electromotive series

TABLE 1

*Intensity of removal of four added cations by fractional electrodialysis from a composite sample of Hyde clay loam*

Results on air-dry soil basis

| PERIOD OF EXTRACTION | K | | Na | | Ca | | Mg | |
|---|---|---|---|---|---|---|---|---|
| *hours* | *m.e.* | *per cent* | *m.e.* | *per cent* | *m.e.* | *per cent* | *m.e.* | *per cent* |
| 0–2 | 1.54 | 56.00 | 0.90 | 24.66 | 0.74 | 17.49 | 0.49 | 11.98 |
| 2–4 | 0.26 | 9.44 | 0.41 | 11.23 | 0.99 | 23.40 | 0.49 | 11.98 |
| 4–6 | 0.16 | 5.82 | 0.40 | 10.96 | 0.69 | 16.31 | 0.64 | 15.65 |
| 6–8 | 0.12 | 4.37 | 0.33 | 9.04 | 0.29 | 6.86 | 0.49 | 11.98 |
| 8–10 | 0.13 | 4.73 | 0.24 | 6.58 | 0.29 | 6.86 | 0.45 | 11.00 |
| 10–12 | 0.11 | 4.00 | 0.35 | 9.59 | 0.29 | 6.86 | 0.42 | 10.27 |
| 12–14 | 0.11 | 4.00 | 0.28 | 7.67 | 0.29 | 6.86 | 0.24 | 5.87 |
| 14–16 | 0.08 | 2.91 | 0.24 | 6.58 | 0.24 | 5.67 | 0.28 | 6.84 |
| 16–24 | 0.10 | 3.64 | 0.38 | 10.41 | 0.22 | 5.20 | 0.24 | 5.87 |
| 24–32 | 0.14 | 5.09 | 0.12 | 3.28 | 0.19 | 4.49 | 0.35 | 8.56 |
| Total extracted | 2.75 | 100.00 | 3.65 | 100.00 | 4.23 | 100.00 | 4.09 | 100.00 |
| Total added | 4.77 | | 4.82 | | 4.22 | | 4.37 | |
| Percentage extracted | 57.65 | | 75.73 | | 100.00 | | 93.59 | |

* m.e. = per 100 gm. soil.

which form stronger ions. The electrodialysis studies of Wilson (20) show that the intensity of removal of cations by electrodialysis is correlated with strength of ions.

### SIGNIFICANCE OF IONIZATION POTENTIALS TO CATION EXCHANGE

In comparing ions with different valence such as magnesium and hydrogen the ionization potential listed by Cooper and Paden (6), and Hodgman and Holmes (13) may be more useful than electrode potentials, as it is desirable to consider the intensity with which the innermost normal valence electron is held. It is interesting to note the position of hydrogen in the atomic grouping where ions are arranged according to the strength of the innermost normal valence electron. Hydrogen follows immediately after calcium and is followed by magnesium in such a grouping. The single valence electron of potassium and sodium, and both valence electrons of calcium are less strongly bound than the single

valence electron of hydrogen, whereas the innermost normal valence electron of magnesium is more strongly bound than the single valence electron of hydrogen. This one property is very probably an important factor in the predominant effect of the hydrogen ion over the magnesium and other relatively weak ions in certain reactions in soil colloidal complexes.

The values in equivalent volts representing the relative intensity with which the different valence electrons are bound are as follows: potassium, 4.33; sodium, 5.15; calcium, 6.90 and 11.78; magnesium, 7.58 and 15.03; and hydrogen, 13.54. Since the single valence electron of hydrogen is less strongly bound than the innermost normal valence electron of magnesium, it might be expected that the hydrogen ion would be relatively more effective than magnesium in conducting an electric current in certain soil electrodialysis studies.

### RELATION OF SOLUBILITY OF MAGNESIUM COMPOUNDS TO AVAILABILITY OF MAGNESIUM AND ITS LOSS IN DRAINAGE WATER

Since the intensity of the removal of magnesium from the soil colloids by electrodialysis is relatively low, it is of interest to note the effect of the presence of certain materials forming soluble magnesium compounds upon the removal of

TABLE 2

*Molar solubility of various magnesium compounds*

| COMPOUND | MOLAR SOLUBILITY |
|---|---|
| Magnesium acetate, $Mg(CH_3COO)_2$ | Deliquescent |
| Magnesium chloride, $MgCl_2$ | 5.76 |
| Magnesium bromide, $MgBr_2$ | 5.25 |
| Magnesium iodide, $MgI_2$ | 5.03 |
| Magnesium nitrate, $Mg(NO_3)_2$ | 5.00 |
| Magnesium sulfate, $MgSO_4$ | 2.88 |
| Magnesium carbonate, $MgCO_3$ | 0.01 |
| Magnesium oxalate, $MgC_2O_4$ | 0.0027 |
| Magnesium fluoride, $MgF_2$ | 0.0014 |
| Magnesium hydroxide, $Mg(OH)_2$ | 0.0002 |

magnesium from the soil. Table 2 includes the relative molar solubility of different magnesium compounds. The high rate of solubility of acetate, chloride, bromide, iodide, nitrate, and sulfate suggests the possible effect of these materials in enhancing the removal of magnesium from the soil. It was observed by Wilson (19) that the addition of chlorides to the soil enhances the removal of magnesium. The relatively low solubility of the magnesium hydroxide probably accounts in part for the relatively small amount of magnesium removed from soils by electrodialysis as compared with the quantity removed by extraction with neutral salts such as chlorides and acetates, which form highly soluble magnesium salts. Carolus (2) found that an application of magnesium to a soil known to be deficient in magnesium significantly increased the yield and magnesium content of vegetable crops. He noted that applications to the soil of

different calcium compounds depressed the magnesium content of plants in proportion to the availability of the calcium compounds applied. Garner (10) found that additions of sulfates and chlorides to the soil markedly aggravated the magnesium-deficiency symptoms in tobacco.

The percentage of red leaves of cotton plants, which showed magnesium-deficiency symptoms (table 3), illustrates the relation of the solubility of magnesium compounds to the magnesium deficiency in crops. The relation between the magnesium-deficiency symptoms in cotton and the source of nitrogen is very probably due to the difference in solubility of magnesium salts formed by the addition of the various nitrogen carriers. The soluble magnesium compounds appear to be readily removed from certain soils in the drainage water, and this may result in a deficiency of magnesium for certain crops. Where nitrates are added to the soil, some magnesium nitrate is formed by reaction with the magnesium. Likewise when soluble sulfate is added to the soil, there may be con-

### TABLE 3

*Relation between magnesium-deficiency symptoms in cotton plants and the source of nitrogen fertilizers, South Carolina Sandhill Experiment Station, 1932*

| SOURCE OF NITROGEN | RED LEAVES ON PLANTS, AUGUST 11 |
|---|---|
| | *per cent* |
| Sodium nitrate | 28.3 |
| Cal-nitro | 24.5 |
| Ammonium sulfate | 24.2 |
| Calcium cyanamid | 24.2 |
| Urea | 20.3 |
| Ammoniated superphosphate | 18.4 |
| Ammo-phos | 2.7 |
| Ammonium sulfate plus basic slag | 1.0 |

siderable loss of magnesium as magnesium sulfate. Where ammonium phosphate was added, only 2.7 per cent of the leaves showed magnesium deficiency. This is ascribed to the formation of magnesium ammonium phosphate, which is only slightly water soluble and prevents the leaching of magnesium from the soil.

### INTENSITY OF ABSORPTION OF NUTRIENT IONS BY PLANTS

There is apparently a marked differential in the intensity of absorption and assimilation of nutrients by plants. Mineral nutrients are not absorbed by plants in the same proportion in which they occur in the soil solution. Beeson (1) showed that there is a wide difference in the mineral composition of plants. It has been suggested by Cooper (4–8) that in general the mineral content of plants is correlated with the relative strength of the nutrient ions. As the magnesium ion is much weaker than the calcium ion, it is logical to expect much less magnesium than calcium in most plants.

Since it is very difficult to determine the difference in intensity of absorption

of mineral nutrients, an indirect approach to this problem is often necessary. It may be logical to assume that under certain conditions the intensity of removal of nutrient ions from soils in electrodialysis studies would be correlated with the intensity of their absorption. It has been shown by Hoagland *et al* (11, 12), Cooper and Blinks (9), and Osterhaut (16) that plants differ markedly in the ions which they selectively absorb. Because of the wide variety of conditions determining the intensity of absorption of nutrient ions, such as permeability of root membrane, utilization of ions, and formation of insoluble compounds in the plant, it is very difficult to determine the initial order of intensity of absorption of ions by different plants. It is believed, however, that fractional electrodialysis studies of plant tissue may serve to establish some of the general relationships between the relative strength of ions and their intensity of absorption, mobility in tissues, and utilization by plants. The data from fractional electrodialysis studies of plant tissue by Cooper, Paden, and Smith (7) show the same order of intensity of removal of cations as was found in the soil studies. The establishment of correlation between such properties as the oxidation-reduction potential values, the ionization-potential values, and the intensity of removal of cations from soil and plant tissue may be very useful in soil and plant nutrition studies. As there is apparently a close relationship between the intensity of removal of nutrient ions from soils by electrodialysis and the intensity of their absorption by plants and also the quality of radiant energy required for assimilation of certain nutrient salts, some oxidation-reduction reactions occurring in growth processes may be of special interest.

## RELATION OF STRENGTH OF NUTRIENT IONS TO QUALITY OF LIGHT UTILIZED IN PHOTOSYNTHESIS

Since there is apparently a close correlation between the strength of ions and the intensity of their absorption by plants, it would seem logical to expect that there would be a close correlation between the relative strength of ions required by plants for optimum growth, the quality of light required for their assimilation, and the food value or quality of energy supplied in the digestion and utilization of the organic compounds which they contain. Cooper (4, 7) has discussed some of the important energy relationships represented by the light-absorption bands of chlorophyll that are in close agreement with the free energy decrease in the formation of certain common nutrient salts and with the energy required for the reduction of common nutrient anions such as nitrates, borates, carbonates, and phosphates.

Since magnesium seems to be more abundant in oily seed than in starchy seed, it may be logical to assume that the utilization of a relatively large quantity of magnesium ions where the other stronger metallic ions are limited would favor the assimilation of hydrogen and the formation of hydrocarbon compounds. Magnesium is one of the constituents of chlorophyll, and a deficiency of this nutrient results in a reduction in the formation of chlorophyll. The quality of radiant energy absorbed by chlorophyll suggests that magnesium is the strongest metallic cation that could be readily assimilated in combination with such rela-

tively light stable anions as carbonate and phosphate. Since there seems to be a definite relation between the free energy decrease in the formation of nutrient metallic chlorides and the absorption bands of chlorophyll, it is interesting to note that the equivalent energy involved in the formation of magnesium chloride is identical to that involved in the reduction of the carbonate ion: 2.85 Volt-Fara-days, equivalent to 4,332 A., or violet-colored light. One of the most distinct light-absorption bands of chlorophyll is in close agreement with these values.

### RELATION OF CLIMATE, SOIL TYPE, FERTILIZER, AND LIMING PRACTICES TO MAGNESIUM DEFICIENCY

The light sandy loams in the humid regions are among the first soils to exhibit serious deficiency of available magnesium. The relatively low magnesium content in these soils and the removal of magnesium in the drainage water result in the appearance of magnesium deficiency in a number of crops. The application of large quantities of fertilizer materials, particularly those containing a relatively large amount of nitrate, chloride, or sulfate, increases the solubility and enhances the removal of magnesium from soils by the drainage water.

Since Garner et al. (10) pointed out the significance of magnesium in the nutrition of tobacco, there has been much interest in the effect of magnesium on the nutrition of many crops grown on the sandy loam soils in the humid sections of the country.

Numerous investigators have reported on the need for magnesium in the production of tobacco, potato, cotton, and vegetable crops. Willis (18) has compiled a comprehensive bibliography on the minor nutrient elements.

After Wheeler and Hartwell (17) showed that application of magnesium salts to certain Rhode Island soils was beneficial to several crops and that one application of dolomitic limestone would supply the magnesium requirements for a number of years, the application of dolomitic limestone became one of the standard soil treatments. Dolomite is satisfactory for many crops with a long growing season, particularly those making optimum growth at relatively high soil pH levels. The quantity of dolomitic limestone added is determined by the pH value of the soil to be used for the production of the different crops. An application of calcitic lime to a soil aggravates the magnesium deficiency. At least two more or less distinct reactions may occur: first, the repressing effect of the basic calcium compound on the hydrolysis of the magnesic complexes in the soil, as pointed out by MacIntyre (14); and second, the selective absorption of the stronger calcium ions by the plants.

A ton per acre application of dolomitic limestone broadcast will supply the magnesium requirements for a number of years. The use of dolomite in the production of non-acid-forming complete fertilizers will usually supply the annual requirement for magnesium for most crops.

Where it is desirable not to change significantly the reaction of the soil for crops with a short growing season, such as bright leaf tobacco and certain vegetable and ornamental plants, soluble magnesium compounds can be used to supply the required amount of magnesium. For rapidly growing crops with a

short growing season, an annual application of the equivalent of 20 to 30 pounds of magnesia in the form of sulfate of potash-magnesia, magnesium sulfate, or Kieserite is the most satisfactory treatment where there is an acute deficiency of available magnesium in the soil. Where water-soluble magnesium salts are used, it may be necessary to make annual or frequent applications as the soluble magnesium salts may be leached from the soil.

## SUMMARY

Magnesium is one of the essential elements in the growth of plants. It is usually present in sufficient quantities in most soils; however, the sandy loam soils in humid regions may not have sufficient available magnesium for the optimum growth of many crops.

Many plants apparently selectively absorb the relatively strong ions, and the quantity of magnesium in most plants is significantly lower than the potassium or calcium content.

The standard electrode potentials, ionization potentials, and the solubility of magnesium compounds are useful in interpreting the behavior in the soil colloidal complex and the absorption by plants of magnesium.

Magnesium is the strongest metallic constituent of chlorophyll. The quality of radiant energy available in sunlight and the quality of radiant energy absorbed by chlorophyll suggest that magnesium is one of the strongest metallic cations that could be readily assimilated in combinations with such relatively light-stable anions as carbonate and phosphate. The magnesium requirements of most soils can be supplied by a broadcast application of a ton or more per acre of dolomitic limestone, which will supply the magnesium requirement for a number of years. The use of dolomite in the production of non-acid-forming complete fertilizers will usually supply the annual magnesium requirement for most crops.

Where it is desirable not to change significantly the soil reaction for such crops as bright leaf tobacco and certain vegetables and ornamental plants, an application of the equivalent of 20 to 30 pounds of magnesia in the form of sulfate of potash-magnesia, sulfate of potash, or Kieserite is the most satisfactory treatment for acute cases of magnesium deficiency. Where water-soluble magnesium salts are used, it may be desirable to make annual or frequent applications as the soluble magnesium salts may be leached from the soil.

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# THE RÔLE OF MANGANESE IN AGRICULTURE

J. S. McHARGUE

*Kentucky Agricultural Experiment Station*

Manganese is one of the so-called minor chemical elements, which in recent years has been shown at this experiment station and elsewhere to have important functions in the economy of soils, plants, and animals.

Manganese is as widely distributed as iron in nature but occurs in much smaller quantities than iron in rocks, soils, plants, and animals. Previous to 1774 compounds of manganese were mistaken for those of iron. In that year Scheele (25) showed that pyrolusite, the most abundant compound of manganese, is the oxide of a new and altogether different metal from iron. Scheele conveyed the information of his discovery to J. G. Gahn, a friend and contemporary who was a skillful metallurgist and who isolated the metal in 1788. Scheele (25) proved that manganese is a constituent of rocks and soils. He also determined that it is assimilated by plants that grow in the soil, because he found manganese in the ash of all the plants he examined. Apparently, he made no effort to ascertain whether manganese performs a useful function in the economy of plants.

In 1864, 90 years after Scheele had shown that plants assimilate manganese compounds when grown in the soil, Sachs (24) proved that the element cannot replace iron in the growth of plants. He failed to show, however, that manganese is also necessary for the growth of plants when iron is present in an available form.

With the development of new and more delicate research apparatus and methods of chemical analysis, it has been demonstrated that about ten of the so-called minor chemical elements which were formerly considered of no importance to plant and animal life, are essential for the growth and physiological well-being of living things.

Previous to 1912, contamination undoubtedly was the principal barrier to the progress of botanists, plant physiologists, and agricultural chemists in revealing the number of essential chemical elements in the economy of soils, plants, and animals. The writer began research on the occurrence and distribution of manganese in nature in the latter part of 1912 and published his first paper on the subject in 1914 (6). In preparing manganese-free cultures, the writer soon realized that chemicals labeled "c.p." are not sufficiently pure for researches on minor elements.

Chemical compounds, however, are by no means the only sources of contamination which have led investigators astray in this field of study. The culture media, either sand or water, the pot or container, distilled water, and dust particles are all possible sources of contamination in minor element investigations and present difficulties which must be eliminated in careful work. Even though these sources of contamination are well controlled, we are still confronted with the fact that viable seeds from which plants are to be grown contain enough of the

minor elements for germination and growth to the seedling stage. Consequently, this reserve of manganese or of any other element under investigation must be taken into consideration and the plant be grown through the important stages of florification, fructification, seed production, and maturity. The viability of the seeds produced must be tested and the different parts of the mature plant analyzed for the presence of the element under investigation. Only with strict observance of accepted research procedures is it possible to ascertain which of the so-called minor chemical elements are essential.

Thus far, more than 20 papers (1, 6–23, 27–30) pertaining to manganese have been published from this laboratory in standard journals of research. Meantime, many other valuable contributions on the subject have come from numerous laboratories (2, 3, 4, 5, 26, 31).

From the results obtained in our laboratory and elsewhere, the following conclusions may be drawn in regard to the essential nature of manganese in agriculture:

The theory that only ten of the chemical elements are essential in the economy of plants and animals has been shown to be erroneous.

Manganese is an essential element in the economy of soils, plants, and animals.

Some areas of soil are deficient in manganese and therefore produce crops inferior in quantity as well as in food quality.

Manganese may be made unavailable in some soils by the application of an excess of basic materials, including calcium carbonate, in the form of ground limestone, marl, hydrated lime, or burned lime.

When some soils are made alkaline with a basic material, the active compounds of manganese are rendered so inactive or unavailable that growth of the crop is retarded, yields are diminished, and the quality of the harvested product is inferior.

The condition on oats known as "grey speck" is due to manganese deficiency or unavailability in the soil.

When different species of plants are grown on the same type of soil they show a considerable range in manganese content. The leguminous plants usually contain the least amount of manganese, and the grasses the greatest amount.

When soybean plants were grown for 18 days in water culture experiments controlled near pH 4.8, it was indicated that high concentrations of soluble manganese in the plant tissues were associated with low concentrations of soluble iron and *vice versa*. Other minor elements, including copper, nickel, and cobalt have similar effects on the concentration of iron in the tissues of plants.

Manganese is an essential element in the metabolism of small animals, including mice, rats, and poultry.

The manganese content of cow's milk can be doubled by adding about 50 gm. of manganese sulfate to the daily ration of the cows. Since the manganese content of normal cows' milk is usually rather low, the question may be asked: Is the increased manganese content of the cows' milk due to feeding inorganic manganese sulfate as effective as it would be if the cow had increased the manganese content of her milk from eating luxuriant pasture grass, hay, or some

normal palatable plant material containing a relatively large amount of manganese? Is it possible to double the manganese content of milk from feeding cows on pasture, hay, and grain rich in manganese?

There is increasing evidence that manganese is associated with the vital organs in which enzymes, hormones, and vitamins are produced and secreted. It is suggested that manganese in some way acts as a catalyst in the production and secretion of these highly essential products.

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# MOLYBDENUM IN RELATION TO PLANT GROWTH

D. R. HOAGLAND

*University of California*

An impressive array of evidence is now available to support the conclusion that the elements boron, manganese, copper, and zinc are essential for the growth of plants of agricultural interest. At the same time there are many suggestions that still other elements may be indispensable in minute amounts. In recent years evidence has been forthcoming to warrant special consideration of the element molybdenum as an addition to the list of chemical elements essential to higher plants. Earlier studies on Azotobacter and Aspergillus species had already shown that molybdenum has a function in the metabolic processes of some microorganisms. This brief summary is concerned primarily, however, with the present status of evidence bearing directly on the essentiality of molybdenum for the growth of crop plants.

Molybdenum has the atomic number 42 and atomic weight of 96 and is thus heavier than other chemical elements usually assigned to the list of essential elements for higher plants. The distribution of molybdenum in soils and in plant tissues is extremely wide, according to the limited information now available. Ter Meulen examined many kinds of plant tissues and always found molybdenum to be present, although the amounts were minute (12, 13, 14). They varied from less than 0.01 mgm. per kilogram of dried plant tissue to 9 mgm. per kilo in bean and pea seeds. The higher values were characteristic of the seeds of leguminous plants. In a list of materials of plant origin examined by Ter Meulen, only sucrose from white cane and refined peanut oil are recorded as having a zero value for molybdenum. Included in Ter Meulen's studies were a series of analyses of the leaves of numerous species of deciduous trees. These all contained molybdenum, which did not decrease seasonally except in horse chesnut leaves. The reason for the latter decrease was thought to be related to migration of molybdenum to the fruits.

An interesting example given by Ter Meulen of the accumulation of molybdenum by living organisms from media in which the element is present in high dilution is that of Azolla, an aquatic plant, which is said to live in symbiosis with a minute alga. The Azolla contained over 1 mgm. of molybdenum per kilo of dried plant, whereas the canal water in which it grew had only 0.0009 mgm. molybdenum per liter.

Ter Meulen also reports analyses of various soils for molybdenum. In general, productive soils were found to have higher contents of molybdenum than soils of low capacity for crop production. The implication seems to be that molybdenum is a necessary constituent of plants. The relation between the presence of molybdenum in the soil and crop production, however, might be fortuitous and cannot lead to a secure conclusion that molybdenum is an essential element for plant growth.

Dingwall, McKibbin, and Beans (8) found molybdenum to be absent from various crops grown in the soils of several Canadian locations. In one soil, however, molybdenum could not be detected in the soil itself and yet it was found in the tissues of many species of plants grown on this particular soil. Konishi and Tsuga [quoted by Jensen (10)] did not always find molybdenum present in the roots of some legumes, and it could not always be detected in the nodules. If plants could be grown through a normal cycle with their tissues completely free of molybdenum, the view that molybdenum is an essential element would be discredited. But the quantities involved are extremely minute, and assurance that the methods of detection of molybdenum are always adequate seems to be lacking. Dingwall, McKibben and Beans, for example, point out certain complications in the use of spectroscopic technique.

It is clear that proof of the essentiality of molybdenum must be sought in artificial culture experiments subjected to rigorous control. Arnon and Stout (2), following the observation by the former that molybdenum, as well as certain other metals, improved the growth of barley plants in a culture solution supplied with ammonium salts as a sole source of nitrogen, undertook a specific investigation of the essentiality of molybdenum. When tomato plants were grown in a solution containing 11 elements, including boron, manganese, zinc, and copper, but with the omission of molybdenum, deficiency symptoms were developed by the plants after a few weeks. The lower leaves acquired a distinct mottling, different in pattern from that characteristic of any other nutrient deficiency previously studied by similar technique. Curling and necrosis at the edges of the leaves were characteristic of the advanced stages of this deficiency. The deficiency symptoms were prevented by addition of molybdenum to the solution. A concentration of only 0.01 p.p.m. was required for this purpose. Similar evidence of molybdenum deficiency was reproduced in six successive experiments at various seasons. Consistency in the development of the molybdenum deficiency was achieved, however, only when redistilled water and specially purified nutrients were used. In order to exclude a possible secondary influence of molybdenum on the root environment, in which microorganisms are present, some deficient plants were sprayed with a dilute solution of molybdic acid. These plants recovered and resumed normal growth.

With regard to the specificity of molybdenum, it was shown that a mixture of Ti, V, Cr, W, Co, Ni, Al, As, Cd, Sr, Hg, Pb, Li, Rb, Br, I, F, Se, and Be could not substitute for molybdenum. Arnon (2) also noted that the growth of lettuce and asparagus was favorably influenced by the addition to the nutrient solution of seven elements, including molybdenum, even when boron, manganese, copper, and zinc were present in adequate amounts. In view of the other evidence, it is probable that molybdenum was responsible for the beneficial effect of the seven elements added to the nutrient solution as a supplement.

Following these experiments, Hoagland (9), as part of another investigation, carried out culture solution experiments with myrobalan plum seedlings. Though the biological variability of the plants was too great to permit a reliable quantitative estimate of the effect of molybdenum, qualitatively a striking re-

sponse to molybdenum was observed. The leaves of the molybdenum-deficient plants were dwarfed; some developed a diffuse mottling, and many showed light brown areas of dead tissue at the tips and margins.

Recently Piper (11) in Australia offered further evidence for the essentiality of molybdenum in an experiment on oat plants grown in nutrient solutions prepared with specially purified nutrient salts. In the absence of molybdenum, but with boron, copper, manganese, and zinc present, necrotic areas appeared at about the time of the emergence of the panicles. "At first the leaves bent backwards in a sharp but smooth bend, but later a kink developed at the collapsed area and the mid-portion of the leaf dried out to a light reddish-brown color." The data for total yields were not influenced to any marked degree by molybdenum, but the increases in yield of grain in response to the addition of this element to the medium were of large relative magnitude and were considered highly significant. Piper suggested that greater effects of molybdenum on growth should be demonstrable by still further purification of the control medium. A concentration of 0.02 p.p.m. of molybdenum in the nutrient solution was more than sufficient for normal growth.

Brenchley and Warington (7), in a brief communication, said that molybdenum has value in improving the growth and health of lettuce plants produced in a nutrient solution. Bertrand (3, 4, 5), impressed by the view that leguminous plants appear to be particularly high in their molybdenum content, conducted an experiment with peas grown in nutrient solutions. The salts used were not absolutely free of molybdenum, and 1 liter of nutrient solution contained 0.004 mgm. of this element, but an increase of concentration to 0.04 mgm. per liter had a beneficial influence on the development of the peas. There was evidence that a deleterious effect began to appear at 0.6 mgm. per liter. Bertrand also observed that the molybdenum content of plants grown in soil varied in accordance with the molybdenum content of the soil. On a dry weight basis leaves contained from 0.6 to 4.5 p.p.m. of molybdenum.

Bobko and Savvina (5) in experiments with peas grown in water, sand, and soil media found no regularity in nodule development, but in the sand cultures they observed that no nodules were formed in the absence of molybdenum, whereas large numbers were present when this element was added to the medium.

Despite these positive indications of a role of molybdenum in plant growth, symptoms of molybdenum deficiency may fail to develop in certain experiments, even when great care is taken to exclude this element as far as possible from the nutrient medium, as is illustrated by the experience of U.S. Plant, Soil and Nutrition Laboratory. Further information is needed on relative amounts of molybdenum impurities in nutrient media under various conditions of artificial culture.

## MOLYBDENUM DEFICIENCY WITH REFERENCE TO AGRICULTURAL CONDITIONS

The history of research on boron, manganese, copper, and zinc amply demonstrates not only that these elements are of importance to an understanding of the fundamental requirements for plant nutrition, but that they also have in varying degrees assumed an agricultural interest. Evidence that molybdenum can be-

come deficient in a soil is very scanty, yet there are some observations to suggest that molybdenum is not invariably supplied by soils to plants in amounts sufficient to meet the full physiological needs of the crop.

Bortels (6) conducted various plot trials with molybdenum and vanadium. For several leguminous crops, molybdenum response was recognized by qualitative inspection. The yield data, while showing a general trend betokening a molybdenum effect, carry no conviction of statistically significant increases of crop yield, except possibly in one case in which a large percentage increase in production of alfalfa seed was noted. Bortels believed that additions of molybdenum may have a beneficial action on the maintenance yields of legumes in soils which do not receive increment of this element in the course of applications of manure or chemical fertilizers.

In Australia, Anderson (1), following observations on the response of pasture plants in a South Australian ironstone soil to applications of wood ashes, made experiments with various combinations of nutrient elements required in large or minute amounts. A striking response to molybdenum in very small applications occurred. Pot experiments with alfalfa in this soil were also strongly indicative of a molybdenum deficiency in the untreated soil. The application of molybdenum greatly augmented the growth of the plants, and the treated plants were dark green, in contrast to the yellowish or pale green color of the untreated plants. Subterranean clover likewise responded favorably to molybdenum.

In view of earlier results on the effect of molybdenum (or vanadium) on nitrogen fixation by Azotobacter, the possibility has not been disregarded that molybdenum may perform a role in symbiotic nitrogen fixation by legumes. Bortels found some indications of increased nitrogen content of leguminous crops as a result of molybdenum treatment. On the other hand, Konishi and Tsuga [as cited by Wilson (19)] concluded that titanium was the only microelement with an effect on the nitrogen fixation by legumes. Jensen and Betty (10) performed sand culture experiments on alfalfa which suggested that a very small, but not infinitesimal, amount of molybdenum was necessary for optimal growth of these plants. Not only the total yield but also the percentage of nitrogen was depressed as a consequence of a deficiency of molybdenum. In other studies with several kinds of legumes grown in soil, analytical data showed that a markedly greater amount of molybdenum accumulated in the nodules than in the root substance itself. This is in general accord with the results of Bertrand. Jensen and Betty did not find this relationship to be true of the element vanadium. Assuming that molybdenum has a role in nitrogen fixation, they concluded that the amount needed is exceedingly small. They regard it as an open question whether or not molybdenum is essential or merely beneficial for plant growth and symbiotic nitrogen fixation. The few experiments now on record certainly do not provide decisive, or even very strong, evidence that molybdenum is indispensable for fixation of nitrogen by leguminous plants. Yet, as this review notes, there are observations from several sources at least to encourage further research on this question, which is one that possesses basic interest, from both physiological and agricultural points of view.

## TOXICITY OF MOLYBDENUM

According to the investigations of Arnon and Stout (2) by the water culture method, molybdenum is not highly toxic to the tomato plant, in comparison with other elements of a micronutrient character. A 10 p.p.m. concentration of molybdenum was required to produced easily observable injury. Warington (15) studied effects of molybdenum on several solanaceous plants and found that symptoms of toxicity were produced by some of the larger applications of molybdenum; for example, by 2 gm. of sodium molybdate applied to 22 kgm. of a soil-sand mixture. Accompanying the injurious effects were color changes, the shoots of tomato and *Solanum nodiflorum* turning golden yellow and potato tubers reddish yellow. The color changes arose from the formation of yellow globules of a tannin-molybdenum compound. Blue granular accumulations of what was apparently an anthocyanin-molybdenum compound also occurred.

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# SELENIUM IN SOILS, PLANTS, AND ANIMALS

SAM F. TRELEASE

*Columbia University*

Selenium is the only mineral element known to be absorbed by food and forage plants in sufficient amounts to make them lethal when consumed by animals. Though highly toxic to animals, selenium is tolerated by most plants. It accumulates in relatively large amounts in some species, and there is evidence that it may be beneficial to these plants and perhaps essential for their development.

The first account of a disease of horses now known to be a form of selenium poisoning was written in 1857 by Madison. After the settlement of northern Nebraska and western South Dakota in 1891, the disease caused heavy losses of horses, hogs, and cattle, and was referred to as "alkali disease." Peters in 1904 erroneously ascribed the disease to moldy corn; but he reported testimony of farmers that involved sound corn, other grains, and pasturage. In 1922 Lipp wrote that farmers were convinced that forage plants store a sufficient quantity of minerals to cause the disease. Franke in 1929 began a series of investigations of toxic grains that led to the discovery of selenium as the cause of alkali disease. In 1933 Robinson reported the finding of 10 to 12 p.p.m. of selenium in wheat and traces of the element in the soil. Nelson, Hurd-Karrer, and Robinson in the same year reported that wheat grown on soil to which 1 p.p.m. of selenium (as sodium selenate) had been added was highly toxic to rats. In 1934 Beath and his associates (1) reported that some poisonous Wyoming range plants, including *Astragalus bisulcatus*, were capable of storing 1,000 p.p.m. of selenium when growing on soils derived from certain Cretaceous and Eocene shales. This discovery removed any doubt concerning the ability of plants to accumulate toxic amounts of selenium from natural soils, and it pointed to an explanation of heavy losses of cattle and sheep on the ranges of fifteen western states.

For more comprehensive treatments of the selenium problem and citations of the literature, the reader is referred to a number of reviews (14, 16–21, 24).

## DISTRIBUTION OF SELENIUM IN SOILS

Seleniferous soils and vegetation are widely distributed in the western half of the United States and extend into Canada and probably into Mexico (1–11, 15, 17, 28, 29). Wheat containing selenium has been obtained from many other parts of the world.

Available selenium is present in soils that have been derived, for the most part, from rocks of the Permian, Triassic, Jurassic, Cretaceous, and Tertiary systems (1–11, 17), which comprise areas of 80,000, 35,000, 40,000, 300,000, and 200,000 square miles, respectively, in western United States. About 1 per cent of the seleniferous plant specimens have been collected on the Permian, 4 per cent on the Triassic, 6 per cent on the Jurassic, 70 per cent on the Cretaceous, and 10 per cent on the Tertiary. The selenium concentration tends to be uniformly high in the shales of the Pierre, Steele, and Niobrara formations of the Cretaceous (17).

Analyses of 500 soils bearing vegetation containing more than 50 p.p.m. of selenium show that 50 per cent of the soils carried from 1 to 6 p.p.m. of total selenium, 25 per cent of the soils contained less than this amount, and 25 per cent contained more, the maximum being about 80 p.p.m. The average for all soils was 4.5 p.p.m.

Soils that support toxic vegetation are found in semiarid regions, where the rainfall is insufficient to leach out water-soluble selenium compounds. Since some of the soils now producing toxic grain have been in cultivation for 50 years, it is evident that cultivated crops do not significantly reduce the poison in the soil.

There is the possibility of adding selenium to soils through the use of insecticides or impure fertilizers, especially superphosphate and ammonium sulfate.

### SELENIUM-SUPPLYING POWER OF SOILS

The absorption of selenium by a plant depends upon the selenium-supplying power of the soil and the selenium-accumulating power of the plant.

Some soils that contain considerable amounts of selenium are incapable of producing toxic vegetation because the element is present in insoluble or otherwise unavailable forms (11). Chemical analyses of soils for total selenium do not reveal the amounts of selenium available for plant absorption. Adequate methods for soil sampling and for detecting water-soluble selenium have not yet been developed (18). To ascertain the capacity of a certain soil to produce seleniferous vegetation, the various species of plants growing on the soil must be identified and analyzed.

The chemical form of the soil selenium is not definitely known, but it may be chiefly a relatively insoluble ferric selenite (11). Considerably more selenate than selenite may occur in the soil solution (11; 18). Organic selenium compounds, derived from plant decomposition, may also be present (2, 3, 17, 18).

Plants are able to accumulate much larger amounts of selenium from organic compounds in a water extract of seleniferous A. bisulcatus than from a sodium selenite solution of equal selenium concentration (3, 26, 27). Nonseleniferous organic substances, such as various proteins and amino acids and also extracts of alfalfa and string beans, have been found to promote the accumulation of selenium from sodium selenite (26, 27).

The presence of sulfate in the culture solution reduces the absorption of selenate (13) but has little or no effect on the absorption of either selenite (13) or the organic selenium compounds derived from plant extracts (3, 14). Depending on the amount of sulfate present, selenate may be absorbed in either larger or smaller amounts than organic selenium from solutions of equal selenium concentration.

Sulfur-selenium antagonism is not likely to provide a practical means of preventing crop plants from accumulating toxic concentrations of selenium. Most of the naturally occurring seleniferous soils already contain large amounts of sulfates, and field tests have failed to demonstrate that the addition of more sulfur is effective in reducing selenium absorption (17, 18, 19).

## SELENIUM-ACCUMULATING POWER OF PLANTS

Different species of plants exhibit striking differences in their power to accumulate selenium. When rooted in the same seleniferous soil, some kinds of plants absorb only insignificant traces of selenium, whereas other species accumulate relatively enormous quantities (1–11) and are useful as indicator plants in locating seleniferous areas.

Plants that show relatively slight ability to take up selenium include most cultivated crops, native prairie grasses, and many other forage plants. Analyses of 1,000 samples of wheat and wheat products from seleniferous areas (29) showed a maximum selenium content of 30 p.p.m.; only about 1 per cent of the samples contained 10 or more p.p.m., and approximately 95 per cent showed less than 5 p.p.m. Analyses of 21 samples of young wheat in Montana fields in which *A. pectinatus* or *A. bisulcatus* was found growing showed an average of only 1.9 p.p.m. of selenium (7). Only one sample contained as much as 8 p.p.m., and this was in a field in which the *A. pectinatus* had 1,890 p.p.m.

In the crop plants, according to Hurd-Karrer, selenium absorption is directly correlated with sulfur requirement. The Cruciferae absorb about four times as much selenium as the legumes, and the latter about twice as much as the cereals; approximately the same ratios apply to the sulfur requirement. This suggested relationship, however, may not extend to the wild plants (19).

Certain native plants have a capacity for selenium accumulation of the order of one hundred times that of farm crops and native grasses. The average content of the selenium accumulators analyzed is about 800 p.p.m., and the highest is 15,000 p.p.m. The accumulators are known at the present time to include about 23 species of *Astragalus* (vetches) and all species so far examined of *Xylorhiza* (woody aster), *Oonopsis* (a composite related to goldenrod), and *Stanleya* (prince's plume, of the mustard family). Many of the accumulators are abundant and widely distributed, covering vast areas in the West and causing losses of livestock estimated at millions of dollars annually.

Among the selenium-accumulating plants, those belonging to the genus *Astragalus* show the greatest diversity of form and the most extensive geographical distribution (4–7). Field studies have shown so far that 23 of the 226 North American species are selenium accumulators; these belong to 6 of the 29 sections of the genus. The most widely distributed accumulators are *A. racemosus*, *A. bisulcatus*, *A. pectinatus*, and *A. pattersonii*. The nonaccumulators are known to include 81 species, belonging to 20 of the genus sections.

A simple test with germinating seedlings may be used to indicate whether or not a given species of *Astragalus* is capable of accumulating selenium, since 20 p.p.m. of selenium (as sodium selenite) in a culture solution has no observable effect upon the early seedling growth of an accumulator, whereas it completely inhibits root development of a nonaccumulator (25).

Available analyses of selenium-accumulating species of *Astragalus*, collected at various stages of development and on a number of types of soil, point to the conclusion that the vigorous plants always contain selenium, and therefore that they can grow only on soils that contain this element. In considering the few

nonseleniferous samples, it should be borne in mind that the specimens may lose selenium on maturing and especially on drying (4). A compilation of analyses of 385 specimens of *A. pectinatus* shows that none contained less than 10 p.p.m. of selenium; 0.3 per cent contained 10–19 p.p.m.; 0.5 per cent, 20–39 p.p.m.; 4.2 per cent, 40–79 p.p.m.; 14.3 per cent, 80–159 p.p.m.; 17.9 per cent, 160–319 p.p.m.; 23.1 per cent, 320–639 p.p.m.; 21.0 per cent, 640–1,279 p.p.m.; 13.8 per cent, 1,280–2,559 p.p.m.; 4.7 per cent, 2,560–5,119 p.p.m.; and 0.3 per cent, more than 5,119 p.p.m.

When two of the selenium accumulators, *A. racemosus* and *A. pattersonii*, were grown in solution cultures and sand cultures in the greenhouse, the development of these plants was stimulated by selenium (as selenite or selenate) in concentrations of from 1 to 27 p.p.m. (22, 23). The addition of selenium to the culture solution approximately doubled the amount of growth made by the plants. (In various tests the dry yields were multiplied by 1.5, 1.6, 1.7, 1.9, 2.0, 2.1, and 2.8.) These experiments showed that selenium is a stimulating and possibly an essen tial microtrophic element for the indicator plants. In these tests the plants received some selenium from the seeds. To prove that selenium is an essential element, it will be necessary to demonstrate that the plants cannot be carried through several generations on a selenium-free culture solution.

A totally different response was obtained with several of the nonaccumulator species of *Astragalus*, including *A. crassicarpus*, *A. drummondii*, *A. palans*, *A. lonchocarpus*, *A. carolinianus*, and *A. canadensis*. These species, when grown in artificial media, were not stimulated, but instead were poisoned by selenium (23). They were injured by 0.3 p.p.m. and killed by 9 p.p.m. of selenium (as selenite).

Chemical analyses of the plants in artificial culture brought out a marked difference in the ability of the two types of *Astragalus* to accumulate selenium. *A. racemosus* was able to store several thousand parts per million without dwarfing or other injury (23). *A. crassicarpus*, in contrast, was able to accumulate only relatively small quantities.

The greenhouse tests of growth in artificial media have confirmed field observations in showing a physiological differentiation of *Astragalus* species into two groups: selenium accumulators and selenium nonaccumulators. Species of the first group seem to require selenium for their development and so may serve as indicators of seleniferous soil areas. Species of the second group occur on both nonseleniferous and seleniferous soils, since they are neither benefited by selenium nor poisoned by the low concentrations available in natural soils. Physiological response to selenium provides a new approach to an understanding of the phylogeny of the *Astragalus* species.

## SELENIUM CONVERTERS

Native selenium indicator plants play an important part as selenium converters and soil contaminators (1, 2, 3). *A. bisulcatus* and other selenium-accumulating plants absorb selenium from virgin shale soils, convert it into water-soluble forms, and, through decay, return it to the soil in forms available for absorption by all types of plants, including farm crops.

Plot experiments have shown that water extracts of *A. bisulcatus*, if mixed with

crude undecomposed Niobrara shale, enable wheat and other farm crops to absorb toxic amounts of selenium, whereas these crops can absorb only traces of the poison when grown on the same shale without the addition of the extract (2, 3, 14). Crop plants absorb dangerous quantities of selenium if sown on soil prepared by plowing under native selenium-bearing plants. High accumulation of selenium from plant extracts has been shown by means of water cultures and sand cultures (26, 27).

Native grasses and other forage plants, when growing in proximity to selenium-bearing range plants, accumulate enough selenium to make them poisonous to animals, but the same species of plants are essentially selenium-free when grown on uncontaminated shales (14).

### FORM AND DISTRIBUTION OF SELENIUM IN THE PLANT

Selenium present in toxic grain has been shown to be a constituent of the plant proteins, where it apparently replaces sulfur normally occurring in these substances (19).

In native selenium-bearing range plants, such as the *Astragali*, about 80 per cent of the selenium may be extracted freely with water, and the water extract contains only organic selenium (3, 11, 19, 26, 27). The selenium present in the extract diffuses readily through a Cellophane membrane (27), and the dialyzed selenium is accumulated by young corn plants to the same degree as the selenium in the original extract. A crystalline organic substance containing selenium and sulfur and having the properties of an amino acid was isolated from *A. pectinatus*, but the yield was very low (12). Some selenium is volatilized, giving these plants an offensive garlicky odor (2).

Selenium absorbed from natural soils tends to be concentrated in the tops of the plants, especially in the seeds. With selenite in water cultures of corn, the ratio of selenium in the tops to that in the roots is about 1/15; with selenate, about 2/1; and with organic selenium, about 1/5.

Symptoms of selenium poisoning have never been observed in either crop plants or native range plants growing on naturally seleniferous soils; but stunting and other signs of injury may be produced by adding sufficient quantities of selenate, selenite, or organic selenium to the culture medium. Selenium from organic compounds (in water extracts of *Astragalus*) is accumulated in very high concentrations (more than 1,500 p.p.m.) without markedly reducing the growth of corn plants. When equally high concentrations in the plant result from absorption of selenate (with sulfate), growth is greatly stunted. With selenite as the source of selenium, internal concentrations exceeding 300 p.p.m. bring about death of the corn plants. These results indicate that organic selenium in the *Astragalus* extract is present in a detoxified state and is relatively nontoxic even to corn.

### SELENIUM POISONING OF ANIMALS

Two somewhat different types of selenium poisoning in livestock may be distinguished; namely, alkali disease and blind staggers (1, 2, 14, 16, 18). Alkali disease, known only in western South Dakota and northern Nebraska, is a chronic

form characterized by deformation and sloughing off of hoofs (16). Blind staggers, the predominant form of the disease in cattle and sheep on the ranges of many western states, represents an acute type of poisoning which results in death within a short time (2, 18). Both diseases seem to be produced by selenium and are characterized by similar pathology (14, 18).

Selenium poisoning in poultry results in eggs that do not hatch or else give rise to weak chicks with ruffled, wiry feathers (16, 18). Similar abnormalities can be produced by injecting selenium into eggs before incubation.

Naturally toxic grain from farms, artificially selenized plants, and salts of selenium have been used in extensive feeding tests on white rats (16, 18, 19, 20). Food containing as little as 5 p.p.m. of selenium stunts the growth of these animals, and about 20 p.p.m. in the food is lethal. The toxicity of selenium, from inorganic salts or poisonous grain, is markedly reduced when the diet contains a high proportion of protein, especially casein (20). Arsenic compounds, supplied in the water or salt, tend to protect animals against the toxic action of selenium (18). The administration of bromobenzene has been reported to increase the excretion of selenium in the urine (18).

Some insects are very sensitive to selenium. Aphids and other insects are killed by low concentrations in plants, and red spiders and mites are controlled by commercial selenium insecticides. But bruchids and seed-chalcids are capable of completing their life cycles in seeds of *A. bisulcatus* containing 1,475 p.p.m. of selenium.

Prelininary surveys have been made to investigate indications of selenium poisoning in the rural population in parts of South Dakota, Wyoming, and Nebraska (20). Nearly all specimens of urine were positive for selenium and contained from 0.02 to 1.98 p.p.m. Aside from high incidence of symptoms pointing to gastric or intestinal disorder, neuritis, and a few cases of apparent liver ailment, no other evidence of ill health was seen that could be ascribed with certainty to selenium. It is believed that a concentration of 5 p.p.m. in common foods, or 0.5 p.p.m. in milk or water, is potentially dangerous. Relatively few vegetables are raised in the seriously affected areas, and most of the flour comes from distant milling centers. Animal products, such as meat, eggs, and milk, seem to be the most important and constant source of selenium to which the inhabitants of affected areas are exposed.

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# SILICON IN PLANT GROWTH

G. J. RALEIGH

*Cornell University*

Silicon has long been known to constitute a considerable percentage of the ash of plants. That it should play some part in their metabolism was considered by early investigators. Much of the early work had to do with its possible effect strengthening the tissue of the plants and its part in reducing the lodging of grains. At about the same time much work was done to determine its effect on the availability of phosphorus and its possible partial substitution for phosphorus in the nutrition of plants. The effect of silicon in preventing lodging has now been largely discounted. Its effect on phosphorus availability is still a subect for investigation. It would seem that the question of possible substitution of silicon for phosphorus would have to await the solution of the problem of whether or not silicon plays some independent role in the growth of plants.

Sommer (4) improved the growth of rice and of millet and Lipman (2) that of sunflower and barley by the addition of silicon to culture solutions. One of the most striking aspects of their data is the considerable variation in their check plants, which suggested that silicon might not have been excluded in spite of careful precautions.

The writer (3) became interested in silicon as a result of an experience in attempting to grow beets (*Beta vulgaris*) of the variety Detroit in culture solutions in asphalt-painted iron containers. With distilled water, plants grew satisfactorily in concentrated solutions but wilted and made very little growth in dilute solutions made with the same lot of chemicals and a similar source of water. When tap water or distilled water contaminated with tap water was used, plants grew satisfactorily in all concentrations. These observations suggested that impurities in the chemicals and in the tap water were responsible for the improved growth of the plants.

In a pilot experiment, beet plants were grown in asphalt-painted soft glass jars and in the painted iron containers. After 3 weeks the roots of the plants in the glass jars were making good growth and the roots were lighter in color than any of those in the metal containers. This observation suggested that some nutrient was diffusing from the soft glass through the asphalt coating. Trial experiments using 10 p.p.m. of $K_2SiO_3$ left little doubt that silicon from the soft glass was responsible for the increased growth in the glass containers.

In four subsequent experiments solutions of the following composition were made from the dry c.p. salts immediately before use: $NH_4H_2PO_4$, 0.0005 $M$; $MgSO_4$, 0.001 $M$; $Ca(NO_3)_2$, 0.002 $M$; $KNO_3$, 0.003 $M$. Asphalt-painted iron containers and pin-punctured rubber tube aerators were used. The chemicals were selected after lots were compared by growing plants in solutions made from them.

In order to reduce the possibility that the results might be due to impurities in the $K_2SiO_3$ in one of the experiments, the $K_2SiO_3$ used was prepared in platinum apparatus from amorphous $SiO_3$.

In three of the experiments relatively young plants were used. In the fourth the plants had previously been grown in solutions containing Si. In all cases, the response to Si was great. With very young plants grown for 1 month with a total of 19 p.p.m. of Si supplied in four applications, 10 p.p.m. being used initially, the fresh weight of the plants supplied with Si was almost 10 times that of the checks. With older plants previously grown with silicon before the experiment was begun, the ratio was approximately 3 to 1. The need for avoiding glass in experiments with Si is illustrated by an experiment in which young beet plants supplied with pulverized soft glass (Mason jar) at the rate of 3 gm. per liter grew as well as those given 10 p.p.m. of Si supplied as $K_2SiO_3$. Very young plants grown with 1 cupful of finely pulverized white sand to 15 liters of solution made three times as much growth as plants in Si-deficient solutions, but the foliage was dark red, perhaps because of toxicity from some material in the ball mill in which the sand was ground.

The response to silicon in all of the experiments was apparently the same. Plants made rapid growth and had green foliage (including the cotyledons) and straw-colored roots. Plants in solutions deficient in silicon made very slow growth. The roots became slightly darker after about 3 days in such solutions, and very dark after a considerable time. At this stage the roots were often covered with fungi. Fungi could not be found in early stages of reduced growth. On older beets secondary growth of roots was common. Wilting of the outer leaves during periods of high transpiration was one of the early symptoms. These leaves developed anthocyanin along the veins, including the secondary veins. In younger plants the cotyledons turned yellow, and most of them soon died.

The addition of $K_2SiO_3$ to culture solutions caused a slight clouding of the solution followed by the gradual accumulation of a fluffy white precipitate. For several days after the application of $K_2SiO_3$, a milk-like precipitate flowed from the plants when they were raised from the solutions for observation or for the addition of iron solution.

No response was obtained from spraying solutions of $K_2SiO_3$ on the foliage of plants growing in Si-deficient solutions.

An unsuccessful preliminary attempt was made to culture excised beet roots in solutions with and without Si in crude Petri dish-like containers made from asphalt-painted tin cans cut to suitable size. Satisfactory growth was not obtained in either of the solutions.

Cursory unpublished tests by the writer indicate that tomatoes and lettuce may respond to silicon.

Wagner (5), using redistilled water and specially analyzed salts, as well as paraffin coatings for glass utensils used in handling solutions, obtained marked response to silicon (added usually as 70 mgm. of $Na_2SiO_3$ per liter) with rice, and considerable response with barley, cucumber, corn, tomatoes, bush beans, and tobacco. His results with rice are in line with a considerable amount of Japanese work. Barley plants without Si were severely attacked by mildew. In contrast with the writer's experience with beets, young plants grew well with and without

Si for 4 to 6 weeks. Wagner (5), with the thought of avoiding impurities, did not aerate the solutions in most of his work. His use of $CuSO_4 \cdot 5H_2O$ at the rate of 0.5 mgm. per liter is somewhat high when compared with common usage. In most of the work he grew the plants in paraffin-coated glass containers.

## SOME UNANSWERED QUESTIONS

The case for the need for silicon for plant growth seems strong, especially in view of the fact that in experiments reported to date the exclusion of silicon has undoubtedly not been so complete as in most work with other elements. It is difficult to obtain chemicals that do not contain considerable silicon, and difficulties involved in attempting to purify or recrystallize chemicals so as to eliminate silicon are involved, as Wagner (5) found. The other two common sources of impurities in culture solutions, namely, the containers and the water, both offer much difficulty in experiments with silicon. In the latter case, these are well illustrated by the considerable attention being given in the chemical engineering literature to deposits of silicon compounds on steam turbine blades. Another commonly mentioned source of contamination with silicon—dust on the foliage —is not, in the writer's opinion, a major difficulty. He holds a similar view concerning the air used for aerating solutions, provided the simple precaution of straining the air through cotton is practiced if there is any question concerning the source of air.

The frequent reference to fungi on plants grown in solutions deficient in silicon raises the question of cause and effect. It is not possible to be sure that fungi grew on Si-deficient roots because the roots grew poorly and offered a good food supply for fungi. It is possible that silicon compounds in the solutions with added silicon discouraged the growth of fungi and this allowed the plant to make satisfactory growth. Sterile culture of excised roots should offer at least a partial solution. Growing plants as did Barker and Broyer (1) should also be helpful, but it would be a complicated task in silicon-free containers.

The precipitate that collects on the roots of beets following the addition of $K_2SiO_3$ to culture solutions may conceivably play some part in the nutrition of the plants. Because of the chemical properties of silicon, it seems unwise to speculate on the nature of such precipitates. The possibility that the precipitate takes toxic materials out of the solution seems improbable, but is not entirely precluded.

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# SODIUM AS A CROP NUTRIENT[1]

PAUL M. HARMER AND ERWIN J. BENNE[2]

*Michigan Agricultural Experiment Station*

The role of sodium in the nutrition of plants has for many years been the subject of controversy. The fact that crops grew and produced in an apparently normal manner in the absence of sodium in the nutrient medium was taken as proof that the element was unnecessary. Until comparatively recently its presence in appreciable amounts in many crops, and in considerable quantites in a few, generally was accepted as incidental, and the element was not credited with having any definite function in the metabolism of the plant.

Numerous theories have been advanced for the apparently beneficial results obtained from the addition of a sodium salt in the fertilization of several crops. Generally the explanation has attributed the benefit to the effect of the sodium ion in increasing the availability or the assimilation of the potassium already present in the soil, in partially replacing the potassium in some of its metabolic functions, or, by some other indirect way, in reducing the potassium requirement of the plant. A few investigators have suggested that sodium might act directly as a plant nutrient, with certain functions which it alone can best fulfill.

It is impossible to make a complete review of all sodium investigations in this short discussion. Instead, the reader is referred to the abstracts made by Willis (14) and to the rather complete bibliography of the foreign investigations by Lehr (10). Atterburg, working with oats, was one of the first to report a yield increase from the use of Na, applied as $NaNO_3$ to quartz sand in a nutritive solution containing varying amounts of potash. He concluded that Na could, in some way, partially replace potassium in the plant and that the Na salts, present in the potash from many of the German mines, were likely to have a definite value in plant nutrition. Studies on the effect of Na, begun in 1894 at the Rhode Island Experiment Station by Wheeler (13) and continued by Hartwell (8) and their associates, are well known to all students of soil science.

In addition to these possible effects of Na in relation to K, several investigators have suggested other possible benefits. Breazeale (1) and Hartwell, Wheeler, and Pember (7) reported an increase in transpiration of wheat when NaCl was added to the nutrient solution. Hoffman (9), as well as the senior author, has observed a decrease in evaporation from the soil resulting from an application of salt. On organic soil, the surface of the salt-treated soil remains more moist, and therefore the soil is not moved by high winds so much as that which has not received a salt application. Osterhout (11) and others hold that sodium, along

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with potassium, has some protective or balancing action which makes it needed in the presence of the antagonizing bivalent ions Ca and Mg.

One of the early causes of interest in the effect of the Na ion on plant growth lay in the comparison of $NaNO_3$ with other carriers as a source of N. Several investigators reported that $NaNO_3$ gave better results because of its Na content. When some other source of Na was added, other N carriers were satisfactory. In this state, celery, produced on organic soil, is one of the heaviest feeders on N, and from 300 to 600 pounds per acre of $NaNO_3$, or its equivalent in some other N carrier, is applied as a side-dressing in two or three applications during growth. Because of its availability and Na content, $NaNO_3$ is usually best for the seedbed. Ammonium sulfate or some other carrier of N can be used satisfactorily in the field if the grower has made a salt application but, without the salt, $NaNO_3$ is likely to be the best source of N.

Hartwell and Pember (8), working with millet, barley, oats, wheat, and rye to determine the effect of Na on transpiration, concluded that the beneficial effect of Na was not due to an increase in osmotic pressure but rather that "sodium was a conserver of potassium." As a result of several years of study, they concluded that: "Apparently certain of the uses of potassium, with some plants at least, may be performed by sodium; although there are certain principal functions of potassium which cannot be performed by any other element. If the amount of potassium is insufficient for the performance of these exclusive functions, probably maximum growth cannot be secured with any amount of sodium which may be added."

### PHYSICAL CHANGES

Several investigators have reported an improvement in color, as well as increased growth of both tops and roots, of the crops under study. Harmer (4), conducting field experiments with organic soil, which is noted for its very low content of Na and K, found that sugar beets receiving NaCl maintained a vigorous, healthy green foliage considerably later in growth and that the leaves of table beets retained their healthier green color, instead of becoming prematurely purple as generally happened when ample K but no Na was applied (figs. 1 and 2). On the organic soil the Na-responsive crops showed less damping-off in early growth and the beet crops less black rot later on, when NaCl was applied along with K. The beet crops showed more resistance to attacks of leaf spot (*cercospora beticola*) and celery to blight (*Septoria Petroselini appli*). The greater gloss on the leaves of these crops suggested a possibly increased waxy secretion which might account for the increased disease resistance. The celery receiving salt was crisper and kept in better condition when exposed on the market.

In order to offer a further comparison of the amount of response to NaCl given by different crops produced under field conditions, some previously unpublished data obtained by the senior author are presented in table 1. The German potash used in the fertilizer mixtures was KCl, containing 50 per cent $K_2O$, and approximately 10 to 12 per cent NaCl as an impurity. Thus the 800-pound-per-acre

application of 0-12-24 contained about 60 pounds of NaCl. This Na impurity apparently was sufficient to satisfy any requirement which parsnips, carrots, and potatoes might have had in the presence of K. Furthermore, the 600-pound
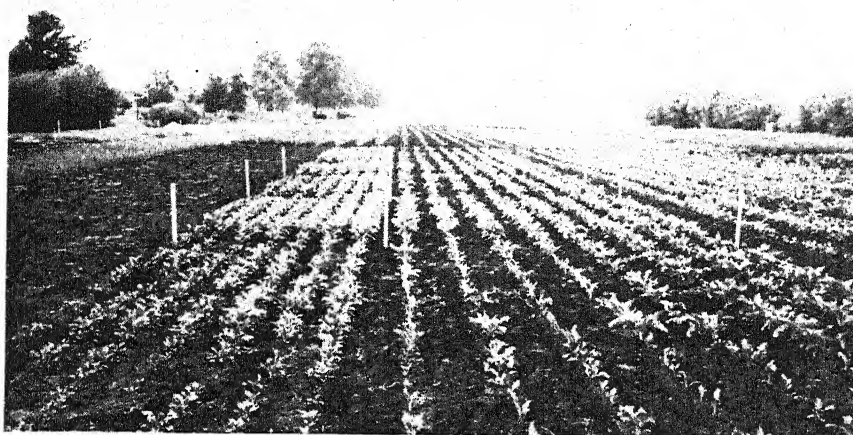


FIG. 1. BEETS SHOW AN EARLY BENEFIT FROM SALT

Table beets (7 rows on left) and sugar beets (8 rows on right) which received 900 pounds per acre 0-8-24 uniformly on all plots, an additional 1,000 pounds per acre of salt between the first and second stakes, an additional 24 per cent of $K_2O$ between the second and third stakes, and 500 pounds of salt just beyond the third stakes.

TABLE 1

*Effect of ordinary salt, when applied with different amounts of potash,\* on yields of several crops grown on Michigan organic soil 1*

| AVE. OF PLOTS | FERTILIZER ANALYSIS,* 800 POUNDS PER ACRE APPLIED ANNUALLY, 1924–1930 | ANNUAL SALT APPLICA- TION PER ACRE, 1924–1930 | YIELD PER ACRE | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Swiss chard (above ground) ave. 2 years, 1928, 1930 | Table beets (roots) 1928 | Sugar beets (roots) ave. 3 years, 1924, 1927, 1930 | Cabbage (solid heads) ave. 3 years, 1926, 1928, 1930 | Parsnips (roots) ave. 2 years, 1928, 1929 | Carrots (roots) ave. 2 years, 1928, 1929 | Potatoes (tubers) ave. 3 years, 1925, 1926, 1928 |
| | | lbs. | tons | tons | tons | tons | tons | tons | bu. |
| 1, 7, 13 | 0-12-0 | 0 | 8.5 | 2.6 | 3.3 | 5.6 | 4.9 | 16.0 | 109 |
| 2, 8 | 0-12-0 | 600 | 20.1 | 5.3 | 5.6 | 7.0 | 4.8 | 15.2 | 110 |
| 3, 9 | 0-12-24 | 600 | 30.9 | 13.7 | 11.5 | 15.5 | 10.1 | 22.6 | 175 |
| 4, 10 | 0-12-12 | 600 | 30.0 | 12.3 | 11.2 | 14.4 | 9.2 | 22.0 | 175 |
| 5, 11 | 0-12-24 | 0 | 25.5 | 9.9 | 9.0 | 14.2 | 10.0 | 23.7 | 182 |

\* German potash used in the mixtures was KCl, containing 50 per cent $K_2O$, and approximately 10 to 12 per cent NaCl as an impurity.

application of salt applied without K failed to produce any increase in yield of these three crops. The beet crops and cabbage, on the other hand, showed an increase with salt both with and without K. The marked increase in yield of

Swiss chard from salt alone suggests that this crop might be able to utilize the Na as a partial replacement for K.  It could not be attributed to any liberation of K in the soil by salt, since the soil was naturally extremely low in this constituent, as evidenced by the low yields of parsnips, carrots, and potatoes when no K was applied.

## CHEMICAL STUDIES

In a study involving the effect of Na on several crops, one of the most striking facts is the great variation in the response to Na by different crops and in the amount absorbed.  Wheeler and Adams (13) found this to be true in some of their
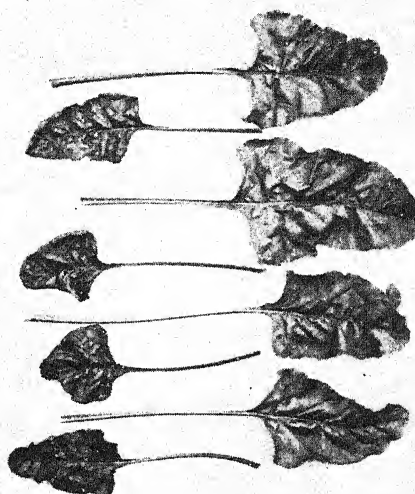


FIG. 2. TABLE BEET LEAVES FROM PLOTS THAT RECEIVED A UNIFORM APPLICATION OF 600 POUNDS PER ACRE OF A 0-8-24 MIXTURE

The plot which produced the small purplish leaves at the left received nothing else, whereas that which produced the healthy green leaves at the right received salt in addition at the rate of 1,000 pounds per acre.

early work, when they decided that corn and squash showed scarcely any effect from Na in the presence of a deficiency of potash, whereas mangel wurtzels gave considerable response.  Lehr (10) compared potatoes, oats, and sugar beets, taking the first as an example of a nonresponsive crop, oats as an intermediate, and sugar beets as a very responsive crop.  Collander (2) pointed out the very great variation in the amount of Na absorbed by different plants and asserted that, in this respect, Na is in a class only with manganese.

The effect of Na on the content of the bases in sugar beets and celery is well illustrated in table 2, calculated from the data in an earlier publication (5) by the authors.  Most striking is the uniformity of the sum of total bases for the various treatments.  Only in the case of sugar beets without potash (treatment 12) was

the total far out of line with that of the other treatments. That plot suffered so much from a physiological breakdown, with decay, that an abnormal total would be expected. With both crops the application of Na resulted in a marked increase in amount of Na absorbed and considerable decrease of K, with some reduction in both Ca and Mg. In the absence of applied K, there was a great increase in absorbed Na, considerable increase in Mg, but no increase in Ca in sugar beets and a further decrease in Ca in celery. It should be mentioned that, with all treatments receiving Na and K, the increase in yield was sufficient to make up for the percentage decrease in K removed in all Na-responsive crops reported in this paper, with the single exception of sugar beets.

TABLE 2

*Yield and basic cation content of sugar beets and celery*

| TREAT-MENT NUMBER | FERTILIZED ANNUALLY, 1932–1937, 600 POUNDS PER A.; 1938, 900 POUNDS PER ACRE | ANNUAL SALT APPLICATION PER ACRE, 1932–1938 | SUGAR BEETS (TOTAL CROP) | | | | | | CELERY (ABOVE GROUND) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Yield per A., ave. 1937, 1938 | Base content per 100 gm. dry matter | | | | | Yield per A., ave. 1937, 1938 | Base content per 100 gm. dry matter | | | | |
| | | | | Ca | Mg | Na | K | Total | | Ca | Mg | Na | K | Total |
| | | lbs. | tons | m.e. | m.e. | m.e. | m.e. | m.e. | tons | m.e. | m.e. | m.e. | m.e. | m.e. |
| 1 | 0-8-24 | 0 | 16.3 | 77 | 80 | 17 | 52 | 226 | 23.0 | 166 | 28 | 27 | 63 | 284 |
| 2 | 0-8-12 | 500 | 22.7 | 71 | 65 | 61 | 29 | 226 | 29.2 | 115 | 24 | 138 | 45 | 322 |
| 3 | 0-8-24 | 500 | 21.3 | 73 | 70 | 68 | 38 | 249 | 30.9 | 129 | 22 | 106 | 59 | 316 |
| 4 | 0-8-48 | 0 | 19.8 | 75 | 72 | 19 | 60 | 226 | 27.1 | 139 | 22 | 36 | 112 | 310 |
| 5 | 0-8-24 | 1,000 | 18.3 | 63 | 50 | 68 | 47 | 228 | 34.4 | 124 | 18 | 130 | 67 | 339 |
| 7 | 0-8-24* | 0 | 20.7 | 83 | 68 | 49 | 43 | 243 | 31.8 | 135 | 20 | 105 | 60 | 320 |
| 12 | 0-8-0 | 500 | 11.1 | 75 | 91 | 107 | 11 | 284 | 13.3 | 110 | 36 | 172 | 16 | 334 |

* Potash applied in form of commercial KCl (60 per cent K$_2$O) in all treatments except 7, where Kainite (20 per cent K$_2$O) was used.

Collander (2), in studying selective absorption of cations by higher plants, grew about 20 different kinds of plants, representing different ecological types, in complete nutrient solutions containing several different cations in equivalent amounts. After about 2 months' growth in this medium, the plants were analyzed for their cation content by spectral analysis. He found that the maximum amount of Na absorbed by any of the plants (by French spinach) was 56 times the minimum absorbed (by buckwheat). The maximum of K absorbed, on the other hand, by one (by corn) of the same group was only 2.8 times the minimum absorbed (by glasswort).

Collander summarizes his findings with regard to Na as follows: "It is evident that among the alkali and earth alkali cations Na is the cation which responds most to specific variations in the plants. This has, in fact, been observed already by van Itallie. In the cell sap of different species of Characeae, Na was found to show a wider amplitude of specific variation than the other cations studied. It is not at all clear, however, why even Na should behave in such a peculiar fashion." He stresses the extremely complex nature of selective salt absorption by higher

plants, and admits that variations among plants in this respect cannot be adequately explained.

The authors (5), in an analysis of 10 vegetable crops produced on organic soil, found the maximum Na absorbed by any of the 10 was 30 times (by table beets) the minimum absorbed (by onions). With an abundance of K available in the soil, only 3.7 times as much K was absorbed by the crop (table beets) absorbing the maximum as by that (onions) absorbing the minimum. They point out that a high Na content of any crop receiving ordinary fertilization indicates a probable

### TABLE 3

*Ratio of potassium to sodium in plants which received an ample supply of both in the nutrient medium*

| PLANT [COLLANDER (2)] (IMMATURE PLANTS) | RATIO K/Na | PLANT [HARMER AND BENNE (5)] (MATURE PLANTS) | RATIO K/Na |
|---|---|---|---|
| French spinach (*Atriplex hortense*) | 0.43 | Celery | 0.78 |
| Seaside plantain (*Plantago maritima*) | 0.74 | Table beets | 0.91 |
| Glasswort (*Salicornia herbacea*) | 0.88 | Sugar beets | 1.17 |
| Halberd-leaved orache (*Atriplex litorale*) | 1.07 | Turnips | 1.66 |
| White mustard (*Sinapis alba*) | 1.65 | Rape | 2.48 |
| Spring vetch (*Vicia sativa*) | 2.56 | Cabbage | 3.21 |
| White sweet clover (*Melilotus albus*) | 2.62 | Kale | 3.59 |
| English plantain (*P. lanceolata*) | 3.19 | Kohlrabi | 4.82 |
| Lettuce (*Lactuca sativa*) | 4.21 | Onions | 12.60 |
| Tomato (*Solanum lycopersicum*) | 4.29 | Asparagus | 13.39 |
| Common poppy (*Papaver somniferum*) | 4.63 | | |
| Spinach (*Spinacia oleracea*) | 5.00 | | |
| Aster (*Aster tripolium*) | 5.19 | | |
| Oats (*Avena sativa*) | 5.32 | | |
| Tobacco (*Nicotiana tabacum*) | 8.00 | | |
| Saltwort (*Salsola kali*) | 12.31 | | |
| Peas (*Pisum sativa*) | 16.43 | | |
| Mercury plant (*Chenopodium bonus Henricus*) | 25.56 | | |
| Sunflower (*Helianthus annus*) | 34.29 | | |
| Buckwheat (*Fagopyrum esculentum*) | 38.00 | | |
| Corn (*Zea mays*) | 44.29 | | |

marked response to Na. Furthermore, a narrow K/Na ratio indicates a probable Na-responsive crop, and a wide ratio, a non-responsive crop. In order to bring out the marked variation in the K/Na ratio in different plants, table 3, showing the ratios calculated from Collander's and from the authors' work, is presented. The two sets of ratios are not strictly comparable because Collander's plants were grown in nutrient solution for 2 months only, whereas the authors' crops were grown to maturity on organic soil under field conditions. In calculating the latter data, only those plots which received both Na and K were included in the averages.

### DISCUSSION

Most of the European work with Na has been with the sugar beet crop. Lehr (10), who investigated the effect of Na on sugar beets in Holland and has recently

published a series of three papers which summarize to considerable extent the European work on the effects of Na on crop production, concludes as follows:

This paper points out once again that, even though without a specific function, sodium is certainly important from an agricultural point of view. Sodium cannot, of course, be considered as important as potassium, because of the greater physiological value of the latter, but in numerous instances sodium can be applied with advantage. Because the effect of sodium depends on special circumstances and crops, the importance of potassium and sodium changes with the crops. For beet, sodium may almost be considered an indispensable nutrient element, approaching potassium in importance.

Although some investigators have reported an increase in transpiration per plant as a result of the presence of Na in the nutrient medium, the increase in transpiration apparently has not been proportional to the increase in growth of the crop. An increase in transpiration does not harmonize with a decrease in wilting of the crop in hot, dry weather, resulting from the presence of sodium, as reported by other investigators. It is possible, of course, that the supply of moisture available to the plant is greater, when Na has been applied, both because the evaporation from the soil surface has been decreased and because the root system has been increased and is, therefore, very probably more far-reaching. Reports of an increase in transpiration have been limited to those crops which do not benefit from Na in the presence of sufficient K, whereas observations of decrease in wilting have been confined to beets (6) and celery, which show a marked yield increase from Na even in the presence of ample K. The quantites of Na absorbed by these crops when salt is applied suggest the more satisfactory explanation of change in osmotic pressure as a factor which may reduce both transpiration and wilting for this high-Na group.

It is well known that Na is essential to animal life. It is important in maintaining an ion balance in the tissues and in its buffer action in the blood stream; it is necessary in regulating the osmotic pressure within the cells and in the body fluids; and it protects body tissues against excessive loss of water. It is probably a necessary component also in marine plant life. Osterhout (12) has reported that Na is essential to the normal growth of marine algae. An average sample of ocean water contains[3] approximately 42 times as much Na as K, with more than two-thirds of the soluble solids present in the water made up of NaCl. A considerable amount of Na is carried by wind action for some distance inland from the seacoast, and therefore the coastal areas are much higher in available Na content than are the inland soils. Studies in Great Britain[4] have shown that 20 p.p.m. of salt are brought down in the annual rainfall along the seacoast as compared to 5 parts 100 miles inland.

It is in this soil high in salt content to which many types of plants were native that we find several of the most salt-responsive plants. However, not all of these halophytes absorb Na. Dr. E. A. Bessey[5] of this institution says that, physiologically, halophytes should be placed in two groups: those which absorb salt, and

[3] Nelson's Loose Leaf Encyclopedia.

[4] Private communication from U. S. Department of Commerce Weather Bureau, Washington, D. C.

[5] Head of the botany department, Michigan State College.

those which do not but which can withstand high salt concentrations and which were native in the salt soils because there they did not have the competition of the salt-sensitive plant population.     The beet is an example of the first group, asparagus of the second.     A description of the native habitat of a few of the wild ancestors of the most salt-responsive crops, as given by DeCandolle (3), follows:

Beet—In sandy soil and especially near the sea in the Canary Isles and all along the coast of the Mediterranean and as far as the Caspian Sea, Persia and Babylon, perhaps even as far as the west of India.

Cabbage—Found in the rocks by the seashore (1) on Isle of Laland in Denmark, the island of Heligoland, the south of England and Ireland, the Channel Isles and the islands off the coast of Charente Inferceure, (2) on the north coast of the Mediterranean, near Nice, Genoa and Lucca.

Horse-radish—Known in Holland as sea-radish, probably from fact that it does well near the sea, a circumstance common to many of the Cruciferae, and which should be the case with this species, for it is wild in the east of Russia where there is a good deal of salt soil.

Turnip—In the sand on the seacoast in Sweden, Holland and England.   [Probably also] in the whole of Scandinavian peninsula, in Finland and Denmark.

Celery—In damp places from Sweden to Algeria, Egypt, Abysinnia and in Asia from the Caucasus to Beluchistan and the mountains of British India.   [Other authors report wild celery as growing in other parts of the world, including California.   It would appear that the original native habitat of celery has not yet been determined.]

There must be considerable variation in the Na content of the soils in the many localities in which celery grew as a wild plant.    Did that variation in Na content of the soil result finally in a difference in Na requirement of the plants in the different localities?    It would be interesting to compare the Na requirement of plants brought from such widely separated regions.    That there may be considerable variation is indicated by the fact that there is some variation in the Na requirement of different varieties of a crop.    Thus Van Itallie (10) compared several varieties of sugar beets as to their Na requirement and found the maximum Na absorbed to be nearly twice the minimum absorbed.    Harmer[6] compared four varieties of celery as to their growth response to applied salt and obtained increases in yield of 17.8, 25.7, 27.1, and 27.6 per cent respectively.

In table 4 is presented a list of crops tabulated according to their Na requirement as determined by a number of investigators.    The authors realize that there probably are inaccuracies in this list, both because of the meager information available regarding some of the crops and because of conflicting conclusions reached by different investigators.    Such discordant opinions are due, undoubtedly, to the fact that the investigations were conducted on widely scattered soils which varied in their natural Na content, and to the fact that early experiments with culture solutions and sand cultures may have been conducted with impure chemicals.

In this table, column 1 lists the crops which do not give any appreciable yield response to Na fertilization under any conditions.   Column 2 contains the crops for which there has been no need for Na fertilization in the past because farm

[6] Unpublished data.

manures and the 50 per cent muriate of potash used in fertilization contained sufficient NaCl so that the requirements of these crops was amply satisfied. With the advent and continued greater purification of American potash salts, so that the total impurities do not now greatly exceed 1 per cent, the sodium requirements of the crops listed in column 3 and possibly of some in column 2, must be taken into consideration in the future fertilization of those crops on soils naturally low in content of Na.

Column 4 (table 4) presents a list of six crops which have a high Na requirement and which, incidentally, are among the first to exhibit boron deficiency. Five of these crops are classed as halophytes, but celery appears not to have been placed in that group. With the exception of celeriac, all of the crops in column 3 like-

TABLE 4

*Effect of sodium applied as a nutrient on several crops*

| NUMBER | DEGREE OF BENEFIT IN DEFICIENCY OF POTASH | | DEGREE OF BENEFIT IN SUFFICIENCY OF POTASH | |
|---|---|---|---|---|
| | 1. None to very slight | 2. Slight to medium | 3. Slight to medium | 4. Large |
| 1 | Buckwheat | Asparagus | Cabbage | Celery |
| 2 | Corn | Barley | Celeriac | Mangel |
| 3 | Lettuce | Broccoli | Horse-radish | Sugar beet |
| 4 | Onion | Brussels sprouts | Kale | Swiss chard |
| 5 | Parsley | Caraway | Kohlrabi | Table beet |
| 6 | Parsnip | Carrot | Mustard | Turnip |
| 7 | Peppermint | Chicory | Radish | |
| 8 | Potato | Cotton | Rape | |
| 9 | Rye | Flax | | |
| 10 | Soybean | Millet | | |
| 11 | Spinach | Oat | | |
| 12 | Squash | Pea | | |
| 13 | Strawberry | Rutabaga | | |
| 14 | Sunflowers | Tomato | | |
| 15 | White bean | Vetch | | |
| 16 | | Wheat | | |

wise are halophytes. Two of the 14 belong to the parsley (Umbelliferae) family, four to the beet (Beta), and eight to the mustard (Cruciferae) family.

The very great variation in Na content of the soil must be taken into consideration in determining whether Na should be supplied as a fertilizer even for the most responsive crops. Soils along the seashore are certain to be well supplied with Na. Sandy soils and organic soils, remote from the ocean and in regions of fairly high rainfall, may be very low in Na content. A communication[7] from Florida points out that celery on the organic soils of that state, part of which were at one time saturated with ocean water, does not respond to Na. In some areas in Florida, in fact, removal of excess salt is an important problem. In Michigan, salt brine from oil wells flowing into organic soil areas or excessive

[7] Private communication from Dr. J. R. Neller, formerly in charge of Everglades Experiment Station, Belle Glade, Florida.

applications of $NaNO_3$ produce a black heart of celery, a physiological breakdown which appears first at the tips of the newer center leaves, working downward and causing a decay of the heart within a few days in hot weather (fig. 3).

Apparently a considerable number of plants, including the 14 crops listed in columns 3 and 4, table 4, and possibly several other halophytes, have the ability to absorb and to utilize comparatively large quantities of Na in the presence of ample K. The root systems of this group evidently have some special means of selectivity for Na by which this ion is absorbed, to the exclusion of ample K. In this group, Na undoubtedly has definite and specific but unknown functions. In addition to considerably increasing yields, it improves the color of the foliage and the vigor and health of the plant, and makes it more resistant to disease. In
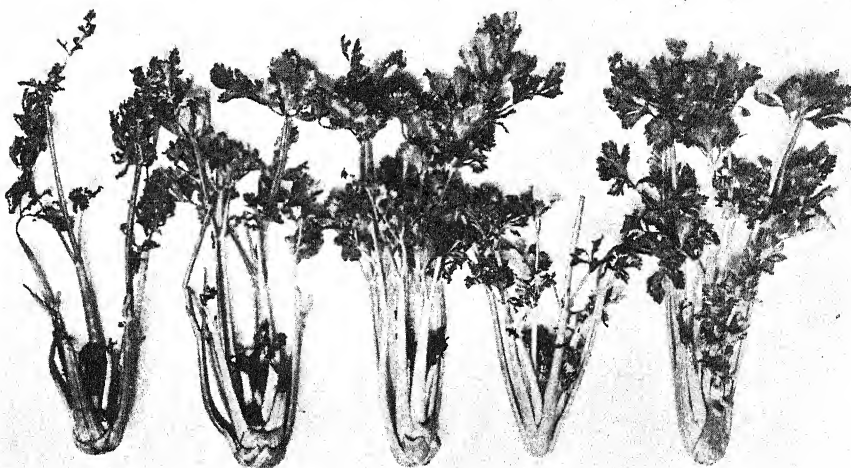


FIG. 3. BLACKHEART OF CELERY APPEARING AS A RESULT OF EXCESSIVE AMOUNTS OF Na, APPLIED EITHER AS $NaNO_3$ OR IN BRINE RUNNING INTO THE ORGANIC SOIL AREAS FROM OIL WELLS ON THE ADJOINING UPLAND

The plant at the extreme right shows the first stages of the physiological breakdown, and that at the extreme left, the last stages.

the absence of known functions of Na in this group of plants, it may be said to be a "conditioner," possibly acting in some ways analogous to its functions in animals. In the absence of Na, it seems probable that extra K is absorbed partly to take care of the unknown functions of Na. In the absence of K, Na is not able to assume all of the functions of K, with the result that a physiological breakdown results.

## SUMMARY

A survey of investigations made in Europe and America regarding the effect of Na on plant growth and the possibility of it serving as an essential plant nutrient brings out the following conclusions:

All crops investigated may be placed in one of two classes, each of which may be subdivided into two tentative groups with regard to their response to Na:

A. Benefited by Na in deficiency of K
  Group 1. None to very slight benefit:
    Buckwheat, corn, lettuce, onion, parsley, parsnip, peppermint, potato, rye, soybean, spinach, squash, strawberry, sunflower, and white bean.
  Group 2. Slight to medium benefit:
    Asparagus, barley, broccoli, Brussels sprout, caraway, carrot, chicory, cotton, flax, millet, oat, pea, rutabaga, tomato, vetch, and wheat.
B. Benefited by Na in sufficiency of K
  Group 3. Slight to medium benefit:
    Cabbage, celeriac, horse-radish, kale, kohlrabi, mustard, radish, and rape.
  Group 4. Large benefit:
    Celery, mangel, sugar beet, Swiss chard, table beet, turnip.

Sodium apparently has no special function in crops which are benefited only in a deficiency of K. It evidently assists with the functions of K.

Sodium appears to have definite functions which it can best fulfill in those crops which are benefited in the presence of ample potash. This is evident in (a) improved vigor of plant and color of foliage, which continues for a longer growing period, (b) increased disease resistance, and (c) decreased wilting in hot, dry weather.

The absence of Na in the nutrient medium of the Na-responsive crops (group 3 and 4) apparently results in an increased absorption of K partly to fulfill the functions of Na. In the absence of K, Na is unable to take over some of the important functions of K; consequently, a physiological breakdown results.

The Na content of the highly responsive crops is greatly increased in the presence of ample Na in the nutrient, whereas K is decreased considerably, and Mg and Ca are decreased slightly. The total K removed in a crop generally is considerably increased, and Mg slightly increased.

The total milliequivalent content of the four bases K, Na, Ca, and Mg remains fairly uniform whether or not Na is supplied as an additional nutrient.

In the proper fertilization of the crops listed in groups 3 and 4, attention should be given to supplying an adequate amount of Na as salt, or in mine-run potash containing Na, or by using $NaNO_3$ if the crops require the N. With further purification of the K fertilizers, it is probably that the Na requirement of group 2 must be taken into consideration on soils which are very low in available Na.

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# SULFUR DEFICIENCY IN SOILS

WILLIAM CROCKER

*Boyce Thompson Institute for Plant Research, Inc.*

## PLANTS THE SOURCE OF SULFUR FOR ANIMALS

Plants, especially green plants, with their great synthetic power, are the ultimate source of sulfur for animals. Though proteins (29, pp. 230–233) are the main sulfur source, other organic sulfur compounds from plants are essential or important in animal economy. The amino acid, cystine, has long been known as a sulfur protein constituent. The tripeptide, glutathione, bearing the amino acid, cysteine, is important physiologically. More recently other organic compounds have been isolated from organisms and identified as sulfur compounds that are essential or important in animal and probably in plant development: the amino acid methionine (22) and the vitamins $B_1$ (34, p. 40) and biotin (21). Higher animals are entirely dependent upon plants for methionine and in part or wholly for nine other nonsulfur amino acids, termed "essential," and mainly for vitamins $B_1$ and for biotin. Vitamin $B_1$ is synthesized in adequate amounts by organisms in the rumen of cattle and to some extent in the intestines of other animals. Synthetic $B_1$ is also used to supplement diets. Ergothionine (21), a sulfur compound of unexplored biochemical function, is found in blood and ergot. Since several physiologically important or essential organic sulfur compounds have been so recently discovered, it is probable that still others will be found. Cystine, methionine, and cysteine as protein constituents exist in every member of every plant family, and the two vitamins $B_1$ and biotin are widely if not universally present in plants.

There are several other organic sulfur compounds (25) found in plants that are limited to certain plant families, and little is known of the significance of these compounds either to plants that synthesize and contain them or to the animals that consume the plants. Members of the mustard family are rich in S-glucosides, sinigrin, sinalbin, and others which, when hydrolyzed, produce mustard oils. Liliaceae (onion and garlic) contain mercaptans, allyl sulfide, and vinyl sulfide. Members of the plant families Resedaceae, Capparidaceae, Umbelliferae, and others synthesize special organic sulfur compounds. Recently it has been shown that organic sulfur compounds (19) of the type of allyl thiourea from the mustard family have goitrogenic action on animals.

Some of the functions of sulfur compounds in animal nutrition (18) may be summarized as follows: The amino acids methionine and cystine are building stones of body proteins; insulin (21), synthesized in the pancreas, is a protein high in cystine; thiosulfate in conjunction with high protein diets often relieves eczema and dermatitis; sulfates mainly from oxidation of proteins play an important role in ion balance of tissues; cysteine in glutathione and perhaps other cysteine complexes play a role in oxidation and reduction processes of the body. Though individual proteins vary greatly in their sulfur content, legumin and zein being

very low and keratin in epidermal appendages like nails and hair very high, Sherman (29, pp. 230–233) points out that proteins of our common foods, both plant and animal, contain approximately 1 per cent sulfur and 16 per cent nitrogen. The fact that plants synthesize so many organic sulfur compounds, several of them known to be essential to plant and animal nutrition and development, puts sulfur in a class with nitrogen and phosphorus as an essential plant and animal nutrient and justifies an inquiry into its possible deficiency in agricultural soils similar to that made for the other two. Although this newer knowledge emphasizes the significance of sulfur as a plant nutrient, the determination of the sulfur content of crops by the Wolff ashing method, which volatilized much of the organic sulfur, misled the early workers on soil fertility into ascribing to sulfur minor importance in fertilizers.

### ERRORS IN ASH ANALYSIS

Bogdanoff was the first to emphasize the importance of sulfur in soil fertility. In 1898 (7, 8) he found that additions of $Na_2SO_4$ to certain black soils of Russia increased greatly the yields of white mustard and some other crops, and this led him in 1899 (7) to determine the sulfur content of crop materials by several methods which showed that the ash in many cases contained only a small fraction of the total sulfur content. For wheat and millet grains and rye bran, less than 5 per cent of the sulfur remained in the ash, whereas for all others the percentage of sulfur remaining in the ash was much higher, and in oat hulls and straw it all remained in the ash.

### EARLY RESPONSES TO GYPSUM

During the last part of the eighteenth century and the first half of the nineteenth, gypsum was used extensively in eastern United States as a fertilizer and generally gave increased yields in certain crops, especially clover. This practice was introduced from Europe, where it got its great impetus from the experiments of the Reverend A. Meyer (12) in the Canton of Berne in 1768. The practice spread later to France and Germany and probably from the United States to Great Britain.

Today little response follows applications of gypsum even to clover and alfalfa in eastern United States. This lack of response in contrast to the response in the early period seems, in light of the present knowledge, to be due to the deficiency of sulfur as a plant nutrient in the soil in the early period and the lack of such deficiency at present. At present the sulfur requirement is supplied in part by the modern use of fertilizers such as acid phosphate and ammonium and potassium sulfates and, of course, manure. As a result of the growth of urban populations and industry, a still greater source of sulfur to crops in the East is $SO_2$ produced by burning coal and other fuels. The $SO_2$ finally reaches the crops in the form of sulfates by being washed into the soil by precipitation or absorbed directly by the soil or vegetation (5). Alway and co-workers (5, p. 237) also offer this explanation for the change in response to application of gypsum to crops in eastern United States. This is in contrast to the early explanation, which held

that gypsum increased crop yields by releasing other nutrients such as potassium in the soil.   The latter explanation seems to have been overworked, as shown by Cubbon (13), Erdman (15), and several other later investigators.   It is probable that soils can be found today in eastern United States that will give great increases in yields of alfalfa and clover due to addition of sulfates.   To find such soils choose partly exhausted soils to which relatively little manure or other sulfur sources have been added and choose land many miles from population centers so there is little sulfur addition from the air.

## SULFUR BALANCE SHEETS FOR SOILS

Dymond, Hughes, and Jupe (14), working at a county farm at Chelmsford, England, were the first to draw up a balance sheet for sulfur as a crop nutrient, considering the sulfur available for crop production from soil content and additions by precipitation and losses by crop removal and leaching.   From this study the authors drew the following conclusion (14, p. 229): "There is not sufficient sulphuric acid in the soil or supplied by rain for heavy yielding crops rich in albuminoid, either for the production of greatest yield or the highest feeding value, and for such crops a sulphate should be included in the artificial manure. For cereal crops and for permanent pasture the soil and rain provide all the sulphuric acid necessary."   Analysis of the top 9 inches of soils in 18 different regions of Essex showed that they always bore less sulfur expressed as $SO_4$ than phosphorus expressed as $P_2O_5$, the average being two fifths as much, whereas the average for crop demands was about equal, expressed as S and P.

A similar balance sheet for sulfur as a crop nutrient was drawn up for Wisconsin soils by Hart and Peterson (17), for Kentucky soils by Shedd (28), for Iowa soils by Brown and Kellogg (10), and for Kansas soils by Swanson and Miller (30), and a similar general conclusion was reached.   The Wisconsin, Kentucky, and Kansas workers emphasized the rapid loss of sulfur from virgin soils after these are put into cultivation.   This they ascribed to rapid decomposition of organic matter and sulfofication and leaching.   With little or no addition of S-fertilizers, Wisconsin soils lose 40 per cent of their sulfur in 50 to 60 years' cultivation, and two to three times as much sulfur is leached from soils at Madison as is added by precipitation.   Hart and Peterson found that Wisconsin soils, per acre foot, contain 1,000 to 3,000 pounds each of S expressed as $SO_4$ and P expressed as $P_2O_5$; that cereal crops, grain, and stover remove two thirds as much of the former as of the latter, alfalfa a little more, and crucifer crops two to three times as much; the average crop of cabbage uses 100 pounds of $SO_4$ per acre year.

Lipman and Conybeare (20) have attempted to make a balance sheet of the principal crop nutrients for the top $6\frac{2}{3}$ inches of the soils of the United States, including crop land, farm pastures, and pastures not on farms—1,445,390,414 acres in all.   They include additions in fertilizers, precipitation, irrigation, seeds and plants, and losses by crop removal, leaching, and erosion, and conclude that net annual loss of sulfur from this land is 3,014,221 tons, or nearly 5 pounds per acre year.   Nearly one fourth of sulfur additions are by irrigation, which is

limited mainly to arid and semiarid lands rich in sulfates.  In all of these lands there are about 649,000,000 tons of P and 378,000,000 tons of S.

Briefly this balance sheet runs about as follows:

*Deposit in soil*—S largely in organic form, less than P.  In United States soils about 60 per cent as much S as P (20).

*Consumed by farm crops*—On the whole, S and P about equal.  For grains (grain and straw or stover), per acre year; corn (100 bushels), S 16, P 23 pounds; wheat (50 bushels), S 10.2, P 16 pounds; alfalfa (8 tons), S 45.9, P 36 pounds; potatoes (400 bushels), S 32.6, P 17 pounds; tobacco (5,000 pounds), S 8.4, P 7 pounds; and cabbage (average crop), S 39.6, P 26.6 pounds.

*Leaching from soil*—S, about 45 pounds per acre; P, none.  *Added from air*—S, as little as 5 pounds per acre year in rural regions and more than 100 near industrial and population centers, in the latter regions the addition being mostly in winter, resulting in great losses by leaching; P, none.

*Added in fertilizers*—In acid phosphate and manure, S and P; and in $(NH_4)_2SO_4$ and $K_2SO_4$, S.

*Deficiencies*: S, in rural regions some distance from population centers; P, general.

### SOILS AT PRESENT SHOWING DEFICIENCY OF SULFUR AS A CROP NUTRIENT

More recently several regions have been found where there is not enough available sulfur in the soil to give maximum yield of legume crops and where additions of sulfur, either in the elemental form or as sulfates, increase the crop yields. The most striking increases are those found in certain soils of Oregon (12) where yields of alfalfa were increased as much as 500 to 1,000 per cent.  It is estimated that there are 250,000 acres in Oregon (26, p. 14) where application of sulfur flour, and sulfur flour seems to be the most effective S-source, will increase the yield of alfalfa 1 ton per acre year.  Tolman and Stoker (33) found both sulfur and nitrogen deficient for maximum production of sugar beet seeds in the soils of the Willamette Valley.  Similar results were obtained in Washington for both alfalfa (23) and peas (16).

In northern Idaho (Sand Point and St. Joe) S-sources give great increases (2) in alfalfa, whereas in southeastern Idaho (Aberdeen) S-sources (32) give little increases and P-sources great increases.  In Montana, S-sources (1) on alfalfa give great increases and higher protein content.  From his analysis of forage plants, Painter (24) concluded that sweet clover and brome and crested wheat grasses grown in North Dakota are deficient in organic sulfur for the nutrition of animals.  The complete absence or extremely low content of sulfates in the grasses indicates that the sulfur supply may limit protein synthesis.  The clover bore considerable sulfates.  Chapman and Brown (11) mentioned the low sulfur content of western soils, found a California soil of granite origin very deficient in sulfur for citrus, but thought that in most cases the deficiency would be supplied from air and by pesticides and fertilizers used on the crop.  Bollen (9) found that on five types of soils tested in Iowa, applications of 200 pounds of gypsum per acre increased the yield of oats and clover in a number of cases, and increased greatly the yields of alfalfa in all cases.  Younge (35) found sulfur deficient for cotton production on ten soil types in Arkansas.  A number of other cases of sulfur deficiency in the United States or foreign countries might be cited.

One of the most interesting and thoroughly investigated sulfur deficiencies reported is that in Minnesota by Alway and co-workers (4, 5, 6). The authors found a belt through the middle of the north half of Minnesota where available soil sulfur was deficient for maximum production of alfalfa, and where the yields of sweet, alsike, and red clover were increased by sulfur additions. Accompanying the increased yield were a deeper green color and a higher S content. Alfalfa showed a greater response than the other three plants and proved best for detecting S deficiency. Stations in the state outside this belt that were tested with alfalfa gave no increase in yields with S additions. The authors made a study of the additions of sulfur from the air in various parts of the state both by precipitation and by direct absorption by soils and plants. They pointed out that galvanized rain gauges give too high values, much S being dissolved from the galvanized surface. Long exposure of the water surface in the gauge to the air gave high values. These errors were especially large where the $SO_2$ content of the air was high. Their studies of absorption of $SO_2$ from the air by soil and specially prepared $PbO_2$ surfaces (protected from rain) led to the realization that direct absorption by soil is a considerable source of S, especially where the $SO_2$ content of air is high, but also measurable and of significance where it is low. In the center of Minneapolis, precipitation brought down more than 100 pounds of S per acre year, with the maximum in winter, whereas in the S-deficient zone only 3 to 5 pounds was brought down per acre year. Where $SO_2$ in the air was high, as in the center of Minneapolis, the amount of S absorbed by the $PbO_2$ surface was several times as high as that brought down by precipitation. In the deficiency belt, less was absorbed by the $PbO_2$ surface than was brought down by precipitation. At Bemidji 3.6 pounds was absorbed, probably higher than that absorbed by a similar surface of soil, and 4.5 pounds brought down by precipitation, both on the acre year basis. The authors mentioned the direct absorption of $SO_2$ by the plant but assigned to it a minor place in supplying the deficiency where the content in the air is low, as is the case where S deficiency exists. On the basis, however, of the ready solubility of $SO_2$ in the leaf, the effectiveness of leaves as gas absorbers, the great leaf surface exposed, and the fact that $SO_2$ is readily transformed to sulfate in the leaf and transported to all parts of the plant and that some is synthesized into organic sulfur, cystine (27, 31), this source of sulfur may be considered of some significance in supplying sulfur deficiency.

On lands in Minnesota where as little as 10 pounds of sulfur per acre year is washed down by precipitation, no response was given by alfalfa with additions of S sources. This may be explained partly by direct absorption of sulfur by the soil and plants and partly by rapid decay of organic matter and sulfofication, through which immediate needs are supplied at the expense of the reserves in the soil.

There is said to be no danger of sulfur shortages in any Illinois soils (3), but when one learns that at the village of Unionville less than 9 pounds of sulfur is brought down by precipitation per acre year, one questions whether the conclusion should not be re-examined for rural regions distant from population centers and railroads.

SYMPTOMS OF SULFUR DEFICIENCY AND FORMATIVE EFFECTS OF SULFUR

Several investigators already cited have found that S-deficiency in soils produces plants with pale green or yellow foliage. Such deficiency in the navel orange (11) caused immature fruits to be yellow-green instead of deep green and mature fruits to be yellow instead of orange, and though it permitted profuse set of flowers, these were weak, and much-deformed fruits resulted. Probably because of lack of sulfur for protein synthesis and growth, N, P, K, Mg, and carbohydrates accumulated in the plants, and the Ca and S content was low. Several investigators have noted low protein content, especially in legumes, as well as poor nodule development in S-deficient soils. It may be that both lack of nitrogen fixation and deficiency of S as a building material account for the low protein of legumes with S deficiency. Under these conditions the value of plants as animal foods is, of course, lowered by reduction of protein content and perhaps other essential organic sulfur compounds. There is need for a study of the quality as well as the quantity of the proteins in legumes under S deficiency. This is especially true of the cystine and methionine content. We should also know how S deficiency affects the biotin and vitamin $B_1$ content. Other symptoms of S deficiency in plants have been observed.

## CONCLUSIONS

There is no doubt of the importance, in plant and animal economy, of sulfur as a synthate for proteins and a number of other essential or important organic compounds. Sulfur undoubtedly is needed in considerable quantities in a number of deficient soils in the United States and other countries, especially in regions distant from industrial and population centers where relatively little sulfur is furnished by the air. Any permanent fertilizer system that does not include the application of a sulfur-carrier is sure to result in sulfur-hungry crops in some rural regions.

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# ZINC AS A NUTRIENT IN PLANT GROWTH

A. F. CAMP

*University of Florida*

Difficulties surrounding the analytical determination of zinc at the levels existing in plants and equal difficulties in freeing water and other chemicals from contamination with zinc have been great deterrents in zinc research, and as a result most of the publications on zinc prior to the last few years have dealt with more or less empirical experiments.[1]  The purpose of this paper is not to answer the basic questions concerning the role of zinc in plants, but rather to point out some phases of the work which are in need of study.   Perhaps zinc deficiency in citrus is somewhat too heavily stressed in this paper, but it has beeen more widely investigated than that in any other crop.

The symptoms now known to be associated with zinc deficiency in many plants were well known long before their cause was determined.   In some plants these symptoms are very sharply defined.   "Frenching" or "mottle-leaf" of citrus and "little-leaf" or "rosette" of deciduous fruits have been the subject of much "pre-zinc" research, and many ingenious theories have been advanced to explain them. The greatest value in these papers is in the listing of the places and conditions under which the symptoms occurred.   As might be expected, some of the conclusions were far afield but many of them have caught the scientific and popular fancy and are still enmeshed in the thinking on zinc deficiency.   It is important that a distinction be made, for instance, between papers on "frenching" and papers on "zinc deficiency" of citrus because of the different viewpoint from which the conclusions were reached.

## HISTORICAL REVIEW

The value of zinc as a plant nutrient and also its toxic effects are not new discoveries, though the extensive use of zinc salts for nutrient purposes on crops in the field dates from about 1931.   Some of the earliest references to the value of zinc as a nutrient occur in the literature on *Aspergillus* spp. about 1900.   Javillier starting about 1907 enlarged this work and by 1912 (13) had been so successful in extending it to green plants that he recommended the use of zinc as a fertilizer material for corn and some other crops.   Maze (16) working at the same time determined by water culture methods that zinc was necessary for the growth of corn, though his work, like that of Javillier, was not well accepted.   Not until the work of Sommer and Lipman (22) and Sommer (23) was zinc widely accepted as a plant nutrient.

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[1] For extensive bibliographies see Willis' "Bibliography of References to the Literature on Minor Elements and Their Relation to Plant and Animal Nutrition," published by the Chilean Nitrate Educational Bureau, Inc., New York; "Hunger Signs in Crops," published by the American Society of Agronomy and the National Fertilizer Association, Washington, D. C.; and for a citrus bibliography, Florida Agricultural Experiment Station Bulletin 335.

As far as the writer knows, the first widespread commercial use of zinc salts in the field was on tung trees in Florida in 1932 and 1933 when several thousand acres were treated. In the period from 1931 to 1936 zinc became established as both a plant nutrient and a valuable fertilizer and spray material. Zinc deficiency symptoms were described for deciduous fruits (5, 6), pecans (1, 7), corn (3, 4), tung (17), and numerous other crops, and by the end of the period zinc was in widespread commercial use on citrus in both California and Florida and on tung in Florida. It is now so widely and successfully used that it is unnecessary to make a case for its utility.

### ROLE OF ZINC IN THE PLANT

Most of the earlier work dealt with symptoms which occurred when zinc was deficient and disappeared when zinc was supplied, and relatively little work so far has involved analyses of the plant tissue. Where such analytical work has been done, the zinc-deficient plants have consistently shown a lower zinc content than healthy plants or those to which zinc has been applied and recovery noted. This is supported by work on pecans by Finch and Kinnison (7), on tung and citrus by Gaddum, Camp, and Reuther (9), on pineapples by Lyman and Dean (15) and others. No cases have been reported in which a plant was found to recover from zinc deficiency without an increase in zinc concentration within its tissues or in which zinc-deficient plants were as high in zinc as comparable normal plants, and there is no evidence of immobilized or inactive zinc within the plant. This would lead to the assumption that zinc-deficiency symptoms result from a simple deficiency in the plant rather than from some indirect soil reaction of the type discussed by Chandler, Hoaglund, and Hibbard (6). The level within the plant at which zinc deficiency occurs and the zinc content of normal tissues appear to vary greatly with different plants. The work of Gaddum, Camp, and Reuther (9) and much more extensive, but unpublished work, by Fudge[2], indicate that a normal citrus leaf might contain from 25 to 50 p.p.m. of zinc in the dry matter, whereas leaves showing distinct deficiency symptoms might contain from 3 to 10 p.p.m. These figures are only approximations to be compared with those of Rogers, Gall, and Barnette (21), who found native weeds growing on old cotton land to contain as much as 700 p.p.m. and averaging as a group 140 p.p.m., while Crotalaria, apparently gorwing normally on the same soil, contained only from 4 to 11 p.p.m. It is obvious that what constitutes a normal content and what a deficient level must be determined for each plant. This line of work has been greatly neglected because of the difficulties involved. The situation is complicated by the fact that symptoms are apparently only those of the final and extreme form of the deficiency, since citrus has been found to decline markedly in production from zinc deficiency long before symptoms appeared. Thus it is difficult accurately to identify "normal" leaves.

The role of zinc within the plant has been widely discussed but at present is mainly a matter of speculation. One common observation probably throws the

[2] B. R. Fudge, associate chemist, Florida Citrus Experiment Station.

most light on this subject. Zinc deficiency in all plants thoroughly studied shows, among other symptoms, some form of leaf chlorosis. The chlorotic areas usually appear between the veins and may vary from white in citrus and corn to light green in some other crops. This simple form of chlorosis may be complicated in some cases by necrosis or the development of a blanketing pigment. If necrosis has not developed, the application of zinc, in such a form that it may be absorbed by the plant, results in the development of green color in the chlorotic areas. Lacking contrary evidence, it may be justifiably postulated that zinc is related to the formation of chlorophyll in some undetermined way. Since the development of the green color has been shown to be associated with an increase in the zinc content of the leaf in every case examined, it would appear probable that the action takes place within the leaf and is not due to some indirect action of zinc on the soil.

The fact that other symptoms such as reduced leaf size, malformation, scant foliage, shortened internodes, and reduced fruit production are associated with zinc deficiency is probably supplementary to insufficient leaf production. Reductions in crop as reported by many investigators from the field and by Reed (20) from water cultures are probably the result of insufficient leaf function. This has not been established definitely, but most investigators seem to agree that reduction in leaf function is probably basic to the other types of symptoms. The exact role of zinc in chlorophyll formation and growth remains to be determined.

### AVAILABILITY OF ZINC

Probably the most interesting and fertile field of investigation is the study of those factors in the plant or soil which result in reduced zinc intake and consequent deficiency. This study involves the behavior of zinc in the soil and its availability as well as several other contributory factors. Many of the theories on this subject are based on restricted observation and do not square with the known circumstances surrounding the occurrence of zinc deficiency.

Identification of the symptoms of zinc deficiency in citrus and their verification by zinc treatment have been reported from California, Arizona, Florida, Australia, New Zealand, South Africa, Palestine, Trinidad, Puerto Rico, and Morocco. The writer has observed the deficiency in Texas and Louisiana, in Cuba, Jamaica, the Bahamas, Honduras, Panama, Colombia, Argentina, and Brazil, and from discussion and correspondence with technical men and producers, is reasonably assured of its occurrence in Bermuda, Spain, Italy, Egypt, India, China, and Japan as well as several other South and Central American countries. It is quite probable that a number of technical reports may have been overlooked by the writer, since citrus literature occurs in many journals of purely local distribution. At any rate, it may be safely concluded that zinc deficiency occurs, in some degree at least, wherever citrus is grown.

The writer and Dr. Vernon Jamison[3] have been collecting information concerning the soils and fertilizer practices associated with zinc deficiency in the

Soils chemist, Florida Citrus Experiment Station.

various areas, and Dr. Jamison has analyzed many samples collected by the writer in areas outside Florida, from which no published data were available, on soils from citrus groves showing symptoms of the deficiency. Published data plus these analyses show that zinc deficiency occurs on heavy clays and clay loams, light sands in which the colloidal material is organic in nature, mucks, soils containing calcium carbonate up to 80 per cent, and clay soils of low exchange capacity. The pH varies from 4.0 in Brazil to 8.5 in Florida and California, but in Florida there seems to be a difference in the character of the deficiency above and below pH 6.0, and observations in Argentina have indicated the same relationship. The soils varied from those extremely high in natural nitrogen to those in Brazil and Argentina, extremely low in nitrogen and receiving no nitrogen fertilization. Occurrence of zinc deficiency was associated with high natural phosphate in California, usually without phosphate fertilization; low natural phosphate in Florida, with and without high phosphate fertilization; and extremely low phosphate in Argentina and Brazil, without phosphate fertilization, the total P often being below 80 pounds per acre-6-inches and the acid-soluble ($0.002 N H_2SO_4$) frequently less than 15 pounds. From these observations it is obvious that zinc deficiency has a relationship to pH, and some have postulated a relationship to nitrogen, others to nitrates, and still others to natural or applied phosphate (24). Except as indicated, the deficiency occurred at all ranges of calcium, magnesium, and potash. It will be seen from this resume that many of the theories are of only local application if they are at all tenable.

Before those soil characteristics which affect directly the availability of zinc are examined, some corollary factors should be discussed, since these are what make the interpretation of soils information of extreme difficulty. There is a profusion of evidence that so far as citrus, and probably a number of other plants, are concerned, anything that affects the root system adversely may result in the appearance of zinc deficiency if the supply of this element is low in the soil. Aftereffects of waterlogging, drouth damage, deep plowing, or even excessive pruning of the top frequently include the symptoms of zinc deficiency. Citrus apparently has difficulty in absorbing sufficient zinc from many soils, and anything that affects the root system adversely is likely to reduce the intake markedly. In connection with root injury, and in other directions also, other mineral deficiencies may have a pronounced effect on zinc deficiency if this element is present in the soil in minimum quantities. Magnesium and copper deficiencies both reduce the root system. When they are acute, zinc deficiency usually shows up, and when they are corrected, zinc deficiency decreases. Fudge[4] has shown an increased zinc content under the latter condition, though no zinc was applied to the soil or sprayed on the tree. Another relationship which is common is found when another deficiency is acting as a limiting factor. In plots in the Argentine on a soil which was deficient in zinc and acutely deficient in nitrogen, the symptoms of zinc deficiency were not acute because of the very limited growth as a result of the nitrogen deficiency. Application of nitrogen in liberal quantities promoted an

[4] Unpublished data.

excellent growth, and zinc deficiency became an acute limiting factor which resulted in a profusion of typically patterned leaves because the supply was insufficient to support a large amount of growth. Conversely, application of zinc without nitrogen resulted in only slight greening of the chlorotic leaves, without the usual vigorous growth response, because nitrogen was deficient. Similar interrelations between magnesium and zinc and between copper and zinc have been repeatedly investigated in Florida. Failure to obtain results with zinc has been found, time after time, to be due to limiting deficiencies of other elements. To what extent similar observations hold with other plants is problematical, but from observation the writer would conclude that the foregoing are basic problems in working with any plant in the field.

In the realm of the soil itself, only one reasonably established relationship stands out, and that is the reduced absorption of zinc as the pH of the soil rises. Floyd (8) in 1917 described typical zinc-deficiency symptoms of citrus as resulting from excessive liming. From 1934 to 1938 the writer and Walter Reuther noted repeatedly that zinc-deficiency symptoms in citrus could be expected when the soil was above pH 6.0 either naturally or because of overliming. Alben and Boggs (2) noted that the deficiency was more severe in pecans that were limed than in those that were unlimed, and recently Fudge[5] in very detailed studies has shown the marked reduction in zinc intake from a uniform application of zinc on sandy soils as the pH increased from 4.5 to above 7.0. Lott (14) showed that zinc toxicity was reduced when the soil was limed to above 6.5. This relationship between zinc deficiency and soil pH has been mentioned by many writers, and it seems reasonably well established that the availability of zinc declines as the pH of the soil rises, the critical point being somewhere between pH 5.5 and 6.5. There is some circumstantial evidence that above pH 7.85 zinc may again become slightly more available and this may be due to the inclusion of zinc in a soluble form in the anion, *i.e.*, a zincate.

The fact that plants which apparently have a high zinc requirement commonly grow on soils of high pH without showing zinc deficiency appears at first glance to invalidate the foregoing conclusion. This reaction is probably related to the presence of large amounts of organic materials. Manures, seed meals, and animal products such as bone meal and dried blood have been widely used as fertilizers, and at least one of their benefits is now known to be their content of highly available zinc and other rare elements. In experiments at Gainesville, Florida, it was found that manure reduced bronzing on tung trees before the use of zinc was discovered; moreover, corn could be grown every year only by the use of very large amounts of stable manure before Barnette *et al.* (3, 4) showed that zinc sulfate could replace it. Natural organic materials were the backbone of Florida citrus fertilization for many years, and reduction in the amounts of these materials in favor of inorganic materials was undoubtedly a large factor in increasing the incidence of deficiencies in Florida. It will probably be found in California that the great advantage which manure was reported to have over

[5] To be published in the Fla. Agr. Exp. Sta. Ann. Rpt. for 1944.

other forms of nitrogen for citrus was at least in part due to its zinc content. In addition to carrying zinc, these organic materials probably form pockets or particles of acid material in the alkaline soils and so retain zinc in an available form. Another factor has been the building up of available zinc in the surface soil by litter from native plants.   This has been reported by Hibbard (10) and others in connection with forest studies; and tung trees in Florida flourished where old hedgerows were cleared, while on adjoining old lands, long devoted to cotton and corn, they succumbed from zinc deficiency, often during the first year.   Rogers, Gall, and Barnette (21) found native weeds high in zinc, often containing several hundred parts per million in the dry matter, and the weeds of a cover crop, as a group, averaging 140 p.p.m., whereas Crotalaria sometimes recommended as a substitute cover in rotations with corn averaged only 8 p.p.m. on the same soil.   This appeared to explain the success of a rotation of corn with weeds on old cultivated land and the lack of success of a rotation with Crotalaria, which apparently had a very low zinc requirement and thus supplied little or no available zinc to the corn. These papers are of basic significance.   Plants apparently vary greatly in their zinc requirements and also in their ability to obtain zinc from a given soil.   Introduced cover crops should be examined with some care as to their mineral content before they are recommended as substitutes for native plants, as the mineral content may be more important than the figures on the tonnage of green matter per acre commonly used.   This field merits much more extended investigation.

The availability problems on acid soils appear considerably more complex. There is apparently the simple deficiency brought on by cropping out of naturally available zinc or that accumulated by native plants as mentioned above.   In such cases the crop plant cannot obtain zinc from the form existing in the soil, though many of the native plants may do so.   The application of zinc to such soils usually corrects the situation, whereas sprays are used on alkaline soils for best results.   On some other acid soils, sprays have been necessary to obtain maximum results and soil treatments are frequently unsatisfactory.   This is particularly true of the acid sands of central Florida.   These have a low percentage of organic matter which constitutes virtually all of the colloidal fraction.   Peech (18, 19) and Jamison (11, 12) have investigated these soils and have found that zinc combines with some of the organic constituents to form very insoluble or very slowly soluble compounds.   These are much less soluble than zinc phosphate and are presumably formed instead of zinc phosphate even when the latter is applied in large amounts.   This is mentioned, since several investigators have theorized, without supporting evidence, that applications of superphosphate were the cause of zinc deficiency in such soils, basing their reasoning on West's (24) findings.   Since no soil extractant has been carefully calibrated to correspond with plant absorption, the data are difficult to interpret.   It is reasonable to assume, however, that the formation of these organic compounds reduces the availability.   The fact that other deficiencies were also present during the earlier work with soil applications makes it almost impossible to evaluate the present situation, since most of the field work was done without eliminating all of

the other deficiencies. Unpublished work by Fudge shows that that trees pick up considerably more zinc and copper when magnesium deficiency is eliminated, but sprays still seem to be more reliable than soil treatments, whereas on citrus at Gainesville and on muck in the Everglades soil applications have been satisfactory. Other plants than citrus have not been extensively investigated on these soils. This line of work needs much more attention, but it emphasizes the necessity of eliminating other deficiencies in a study of zinc deficiency and also the necessity of combining spray treatment with soil treatments in studying zinc deficiencies in other plants and on other soils. The final solution in any case will have to be the close correlation of soil studies with plant analyses.

## SUMMARY

The necessity of many plants for traces of zinc and also its usefulness in the field have been well established.

The role of zinc within the plant is not yet understood, but in the absence of other information it may be postulated that zinc is necessary for chlorophyll formation and growth. The presence of zinc within the plant seems to be fairly well established, and this would tend to eliminate the possibility of indirect action in the soil as the cause of the correction of zinc deficiency.

The availability of zinc varies with the pH, being lower as the pH rises, the critical point being between pH 5.5 and 6.5.

The deficiency of zinc on many acid soils appears to be due to the cropping out of naturally available zinc or that accumulated by native plants and to failure to replace it by proper cover cropping or by fertilizing.

On some acid soils availability may be reduced through combination of the zinc with organic compounds in the soil.

Reduction in the use of organic fertilizers and the replacement of many native covers with cover crops of low zinc requirement plus indiscriminate liming will probably result in greatly increased zinc deficiency in crop plants in the future.

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# MINOR ELEMENTS AND VITAMIN CONTENT OF PLANTS

KARL C. HAMNER

*U. S. Plant, Soil, and Nutrition Laboratory*[1]

There has been relatively little work dealing with the relations between mineral nutrients of plants and their vitamin content. Recent reviews by Maynard and Beeson (20) and Hamner and Maynard (8) have covered much of the literature in this field. These two reviews have indicated that variations in vitamin content of plants are related to many factors, including varietal differences, variations in climate and seasonal differences, and, to a lesser degree, fertilizer practices. The evidence with respect to the influence of fertilizer practices and soil factors was not conclusive. As Maynard and Beeson pointed out, "A critical study of the mass of data dealing with the effect of soil type and nutrient supply suggests that both have much less influence than variety and climate. It is clear, however, that only a few of the many possible relationships have been studied."

In the present discussion, work dealing with the possible influences of the supplies of nitrogen, phosphorus, and potassium is not considered. More work has been done, of course, on the possible influence of these major elements than on that of the minor elements, but even so, the evidence with respect to any one of them is not conclusive. For example, experimental work has shown that under certain circumstances the application of nitrogenous fertilizers may decrease the ascorbic acid content of plants or plant parts. On the other hand, under other circumstances the application of nitrogen may have no effect. The variations in ascorbic acid content associated with seasonal and locational differences may be very great, and evidence is accumulating that variations in the intensity of illumination may possibly be the primary factor in causing these differences (10). If intensity of illumination is the primary factor in determining ascorbic acid levels, then one might expect that under certain circumstances (especially in considering the ascorbic acid content of fruit) the application of nitrogen might result in an increased amount of foliage and, with the resultant shading, cause a decrease in ascorbic acid of the shaded portions. The ascorbic acid content of plants may vary from one end of a small field to another (9), and it is very important to the proper interpretation of results that an experiment be designed in such a way that the influence of treatment may be separated from the influence of other factors which are not under experimental control. The variations in ascorbic acid from one plant part to another and from one plant to another may be large, and care must be exercised in selecting sampling methods. It is usually desirable to have a measure of the sampling error in order to evaluate properly the significance of the final results. In many of the data with respect to ascorbic acid, consideration of the above factors is not evident, and it is difficult to evaluate the data. Since so little is known with respect to the other vitamins, one can only assume

that it would be desirable to exercise the same care in designing experiments and interpreting results that are clearly indicated for ascorbic acid.

The influence of the supply of the minor elements on the vitamin content of plants is of interest in two ways. In the first place, if a definite correlation is found between the supply of some particular nutrient element and the vitamin content of plants it might be possible by fertilizing with this element to increase the nutritive value of the crop sufficiently to make the practice worth while commercially. Secondly, such a correlation would be evidence supporting a physiological relationship between the element in question and the synthesis or metabolism of the vitamins.

Some investigators have analyzed plants for their mineral content and have attempted to correlate the content of particular minerals with the occurrence of vitamins. For example, McHargue (19) in 1924 analyzed a great many plant and animal materials for manganese. He reported relatively high manganese values in materials which were at that time believed to be rich in vitamins (*i.e.,* in the pericarp of barley, wheat, and rice, and in tomatoes and citrus fruit). Randoin and LeGallic (25) reported that the thiamine content of cereals and cereal products varied directly with the iron and protein contents and that in some classes of green vegetables the ascorbic acid and carotene contents showed a similar correlation with iron and protein. Koblic (14) found a high manganese content in plant materials which were also rich in ascorbic acid. Results such as these are, of course, not conclusive but merely serve to indicate the need for critical experimentation. On the basis of the work to date, no justification is evident for relating cause and effect in the foregoing correlations.

### ASCORBIC ACID

Two reports (13, 18) have indicated that the ascorbic acid content of potatoes was not influenced by the addition of minor elements to the soil. In neither of these reports was evidence presented that such an addition improved the productivity of the plants. Wade and Kanapaux (31) and Wade (30) found an insignificant correlation between the ascorbic acid content of the pods and leaves of snap beans and the manganese content of the soils on which they were grown. The authors indicated that manganese was probably not limiting for growth in any case. On the other hand, Hester (11) reported that tomatoes grown in twelve soils low in available manganese were lower in ascorbic acid than tomatoes produced in twelve soils higher in available manganese. He reported that in pot cultures the application of 1 gm. of $MnSO_4 \cdot 4H_2O$ to 15 kgm. of sandy loam soil (pH 7.1) increased the ascorbic acid content of the tomatoes from 142 to 243 mgm. per liter of pulp. Very little detail of the experimental design, sampling techniques, or experimental error is given.

Rudra (27, 28) reported on work which led him to believe that manganese is indispensable for the synthesis of ascorbic acid by animals and plants. In his plant work, he grew seedlings in nutrient solutions containing various amounts of manganese salts and found greater ascorbic acid synthesis when manganese was present than when it was absent. He grew the plants for only a short time and

did not use a balanced nutrient solution. Lyon and Beeson (15) in extensive controlled culture experiments found manganese-deficient tomatoes as rich in ascorbic acid as control plants. The careful design of the experiments and the statistical evaluation of the results seem conclusive. The variations in ascorbic acid found by Hester may not have resulted from the direct influence of the manganese fertilization on manganese supply to the plants but rather from secondary effects of the fertilizer. There is need for more work as to the influence of manganese fertilization on the ascorbic acid content of plants, particularly with respect to soils known to be deficient in this element. The suggestion that the presence of manganese is essential to the synthesis of ascorbic acid in plants is stimulating, but the evidence to date does not seem extensive enough to warrant such a conclusion.

That magnesium fertilization may increase the ascorbic acid content has been indicated by Cowart (4) and Cowart and Stearns (3) for oranges and grapefruit, by Balks and Pommer (1) for cereal seedlings, and by Pfaff and Pfützer (22) for spinach, cabbage, and grass. The last workers found no effect of magnesium on the ascorbic acid content of kohlrabi, tomato fruits, potatoes, and sugar beets. Hamner, Lyon, and Hamner (9) also found no influence of magnesium supply on ascorbic acid in tomatoes. Roy and Bahrt (26) found that oranges from "bronzed" trees yielded juice containing subnormal amounts of ascorbic acid. About 2 years subsequent to the addition of magnesium to the soils, the ascorbic acid content of the fruit was restored to a normal level. The addition of minor elements to trees which appeared normal produced no effect on ascorbic acid content. Hamdallah (7) grew plants in nutrient cultures with and without magnesium. No effects on the ascorbic acid content of bean or corn seedlings were produced by magnesium deficiencies, even though, under such conditions, the plants became very chlorotic. Similar results with turnip greens in sand cultures were obtained by Bernstein, Hamner, and Parks[2]. This evidence indicates that increasing magnesium supply increases the ascorbic acid content of some plants and not of others. Reports that magnesium increases the ascorbic acid content are from fertilizer experiments in soil, and it seems possible that under such conditions the influence of magnesium is not direct but may result from secondary changes in the soil as the result of fertilization.

Hamner, Lyon, and Hamner (9) found that when other nutrients were supplied to the plants in adequate amounts, wide variations in the supplies of calcium, magnesium, and sulfates produced only small effects on the ascorbic acid content of tomato fruit. Deficient supplies of sulfates resulted in slightly above-average ascorbic acid values. Lyon, Beeson, and Ellis (16) grew tomatoes in nutrient solutions deficient in copper, manganese, zinc, iron, or molybdenum. Great decreases in growth and fruitfulness resulted from withholding any one of these elements except molybdenum, and mineral analyses of the plants demonstrated a greatly reduced concentration in the plant of any particular element not sup-

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[2] Bernstein, L., Hamner, K. C., and Parks, R. Q. The influence of mineral nutrition, soil fertility, and climate on carotene and ascorbic acid content of turnip greens. 1944. [Unpublished.]

plied in the nutrient solution. Iron deficiency resulted in a small but significant increase in ascorbic acid in the fruit; no other change in ascorbic acid was related to deficient supplies of these minor elements. Lyon and Parks (17), in a similar experiment, found no influence of deficient supplies of boron on the ascorbic acid content of tomatoes. Hamdallah (7) found no difference in ascorbic acid content between bean and corn seedlings deficient or not deficient in iron. Roy and Bahrt (26) found that oranges were lower in ascorbic acid from "frenched" trees than from normal trees and that upon the addition of zinc to the soil to cure the disease the ascorbic acid content of the fruit returned to normal within 2 years. These results with oranges are in contrast with those of Lyon *et al.* (16) on tomatoes and indicate a possible difference in response of different species.

The influence of excessive supplies of the minor elements (Cu, B, Mn, Zn, and Fe) on ascorbic acid in tomatoes and turnips has been studied in sand cultures by Lyon and co-workers in unpublished work of this laboratory. Each of the minor elements was supplied in the nutrient medium at levels ranging from those which gave normal growth to those which were definitely toxic. Over those ranges of supply which resulted in a considerable decrease in growth and fruitfulness of the plants, copper increased the ascorbic acid content of tomato fruit about 80 per cent; boron, magnesium, and molybdenum resulted in a decrease in ascorbic acid values; and zinc and iron were without apparent effect. In turnip greens grown with similarly high levels of supply of these elements, there was slightly less ascorbic acid when excessive amounts of manganese, iron, boron, and copper were supplied, but no consistent influence of molybdenum was shown on the ascorbic acid. It should be emphasized that in all cases where excessive amounts of these minerals affected ascorbic acid content, the effects on growth and fruitfulness were also very marked, and it is doubtful whether these results will have any practical significance.

Hageman *et al.* (6) found that the addition of potassium iodide to the nutrient solutions supplied to tomato plants growing in sand cultures decreased the ascorbic acid content of leaves and fruit when supplied over a range 4 to 100 p.p.m. of I. Concentrations of 4 p.p.m. of I did not reduce the growth of the plants as measured by their dry weights, but a very appreciable reduction in ascorbic acid occurred in both the fruit and the leaves. Nelson and Mottern (21) reported that oranges sprayed with lead arsenate contained less ascorbic acid than did comparable unsprayed oranges.

### CAROTENE

It is difficult to interpret many of the results dealing with the influence of minor element supply on the carotene content of plants. Most of the work has dealt with the possible influence of nitrogen, phosphorus, and potassium fertilizer elements, and there is no uniform agreement among the various investigators as to the effects of the elements (20). In fertilizer experiments, Whittemore (32) reported no appreciable effect of manganese on the vitamin A value of spinach, and Barnes (2) found no influence of manganese on the carotene content of carrots. Honeywell and Dutcher (12) indicated that chlorotic spinach grown on soils

deficient in manganese contained less provitamin A than did normal spinach. It seems likely that soils sufficiently low in manganese to cause chlorosis will be associated with low carotene values in the leafy crops. These results indicate that fertilization with manganese over and above that needed to prevent visible chlorosis will have little effect on carotene.

Ellis and Hamner (5) studied the carotene content of tomatoes grown in sand culture with many different nutrient solutions. Wide variations in the supply of calcium, magnesium, and sulfates produced no measurable effect on the carotene content of the fruit, even though great variations in growth and fruitfulness of the plants were produced. Lyon, Beeson, and Ellis (16), in work mentioned previously with ascorbic acid, studied the influence of deficiencies of manganese, copper, zinc, iron, and molybdenum on the carotene content of tomatoes. Limited supplies of these elements produced no significant effect upon the carotene content of the fruit. Bernstein, Hamner, and Parks[2] produced turnip greens in soils with many different fertilizer treatments and in sand cultures with numerous different nutrient solutions. No appreciable effect of fertilizer treatment on carotene content of plants grown in soil was noted, even though these fertilizer treatments caused marked influence on growth and development of the plants. In sand cultures, deficient supplies of magnesium, calcium, and sulfates caused a decrease in carotene content with an associated chlorosis. Powers (24) found an increase in carotene content of alfalfa when soils presumably deficient in boron were fertilized with that element. Similar results were obtained by Beeson in unpublished work at this laboratory.

Thomas and Moon (29) found no influence of iron sulfate applied as a fertilizer to grass, but no conclusive evidence was presented that the unfertilized plants were deficient in iron.

Pollard (23) reported that the presence of excessive amounts of chloride in the fertilizer was associated with a low carotene content of carrots.

In fact, a general consideration of the foregoing results indicates that any treatment which caused visible chlorosis of the plants resulted in appreciable decreases in carotene in the leaves. The fruits seem to have a carotene content more independent of treatment than leaves. No consistent relationship between the amount of the growth and the carotene content has been demonstrated.

### OTHER VITAMINS

Very little work has been done as to the influence of minor elements on the content of any of the other vitamins in plants. For the influence of soils and fertilization in general, reference may be made to the review by Maynard and Beeson (20). Lyon *et al.* (16), in connection with previously discussed work, measured the riboflavin content of tomatoes grown with deficient supplies of copper, manganese, zinc, iron, and molybdenum. Only slight variations in riboflavin content were correlated with these deficiencies. The results indicated a possible slight decrease in riboflavin with the fruit from zinc-deficient plants. Lyon and co-workers, in unpublished work at this laboratory, have studied the effects of excessive supplies of copper, boron, manganese, zinc, iron, and molyb-

denum on some of the B vitamins in turnip greens.   Although the analysis of the results has not yet been completed, preliminary inspection indicates that excessive supplies of these elements produced relatively large variations in the content of thiamine, riboflavin, and nicotinic acid.   For instance, 60 p.p.m. of boron in the nutrient medium resulted in a small decrease in the growth of the plants and an approximate increase of 80 per cent in the thiamine content of the greens. Somewhat less striking results were apparent for other vitamins and other elements.   It is anticipated that these results will be published in detail shortly.

## SUMMARY

So little work has been in this field of minor elements in relation to the vitamin content of plants that this review can do but little more than indicate this fact. It seems probable that variations in the ascorbic acid content of plants such as might be encountered under field conditions are influenced so markedly by differences between varieties and by climatic conditions that the possible influence of soil conditions and fertilizer practices will be found to have little practical importance.   It seems probable also that any fertilizer treatment (or lack of treatment) which causes the development of chlorosis in the plants will likely decrease the carotene content of the leaves.   With respect to both carotene and ascorbic acid, it is fortunate from a practical standpoint that results which have been obtained to date indicate that those treatments which are likely to give the highest crop yield per acre are also the ones most likely to give the highest vitamin yield per acre.

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# BIOLOGICAL FUNCTION OF MINOR ELEMENTS

OSKAR BAUDISCH[1]

*Saratoga Springs Commission*

The writer has made an approach to the use of magnetism as a tool to solve biological problems. It is known that magnetic susceptibility data make possible a choice, in many instances, between alternative chemical structures and between alternative bond types. Magnetism is particularly used for the identification of space configuration in the complex ions. Research of this type was first carried out in this country by Baudisch and Welo (2, 12) at the Rockefeller Institute for Medical Research. We made an attempt to link electronic structure of metal complexes to their specific chemical and physical behavior by using magnetic measurements and Roentgen ray spectroscopy. Throughout the present paper the emphasis is placed on experimental results and their significance to structural theories. The apparent but still elusive relation between magnetism and catalysis is approached in a new way.

The experiments of other investigators and our own described in this paper touch the fundamental principles of respiration and penetrate into the obscure realm of biochemical synthesis. Part of the story of the development of life on our planet is its key-use of magnetic oxygen gas. The synthesis of the porphin ring (hemoglobin, chlorophyll) which is so prevalent in plant and animal cells and which increases decisively life's access to the planet's oxygen has followed in the course of evolution. How is porphin made in nature? The writer many years ago introduced a hypothesis, based on experimental research, on how organic compounds are formed from inorganic by the influence of sunlight. A possible formation of the general porphin structure $- N = C - CH = C - N =$ is indicated in the new hypothesis (fig. 1). The writer assumes that nitrosyl, NOH, is the primary reacting nitrogen compound. He also assumes that the nitrosyl radical in an acid or neutral medium reacts like molecular oxygen:

$$O = O \qquad\qquad HON \overset{acid}{\underset{alkali}{\rightleftarrows}} HN = O$$
$$HN = O$$
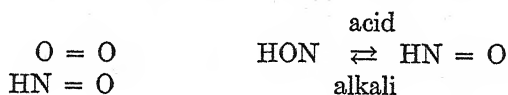
The NH grouping is isosteric with the oxygen atom. Both possess six electrons with probably the same or a very similar spatial arrangement (3, 4, 5, 6).

$HN = O$ will react with monovalent copper, forming a complex in which the nitrogen atom possesses an uncompensated electron and thus becomes a paramagnetic radical, $Cu^1 = \overset{x}{N} = O$.

The reactivity of a paramagnetic nitrogen atom is demonstrated in the paper. It is assumed that protein attached to copper converts nitrogen atoms into micromagnets, as indicated in the formula (see figs. 6, 7, 8). It is known that atoms

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and molecules in biological processes often form functional units in a definite energy state. The presence or absence of metallic ions may greatly influence such units by changing the state of energy of electric or magnetic fields of the unit. The knowledge of common energy levels will help to understand why extremely small amounts of the metallic ions often bring about such pronounced biological effects.
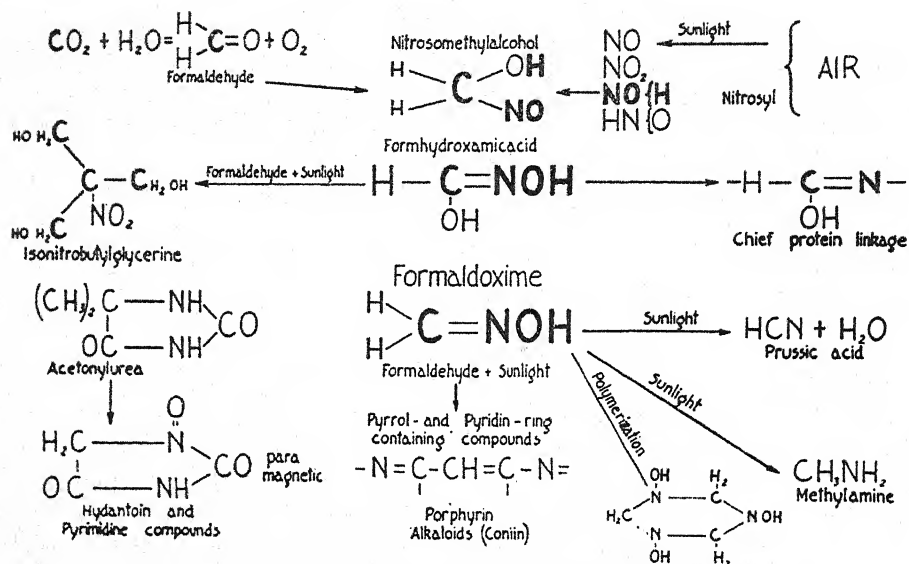


FIG. 1. GEOCHEMISTRY OF CARBON AND NITROGEN

Formation of organic compounds from inorganic by the influence of light.

## GENERAL CONSIDERATIONS

The chemical elements which are considered as important for the living cells can be roughly classified as follows (7):

1) Structural elements (C, H, N, O, P, S, Cl, Na, Mg, Si, Ca)
2) Biocatalysts (Fe, Cu, Co, Ni, Mn, Zn, Mg, As, Mo, Ca, Al, B, and other trace or minor elements)
3) Biogenerators (radioactive trace elements)

To the last group belong $K^{40}$, radium, radon, uranium, and others. Elements of this class are especially highly enriched in the vital organs such as the heart, the mammary and reproductive glands, and the Kupffer cells of the liver. They are speculatively considered as of particular significance in the construction of genes, cell division, and mental and spiritual processes. The elements of this group are important not only because of their direct radiation but also because of their ability to "excite" other elements and make them more reactive.

In this short article the writer will attempt to demonstrate that elements which we have here listed as biocatalysts are also able to "excite" other atoms. This "excitement" may be brought about in many different ways, for instance,

by increasing the coordination number of the reacting atoms or group of atoms, after combining, by rearrangement of the electronic structure and formation of electronic isomeres of atoms and groups of atoms. For example, boron is a minor element of great importance in cell life, which possesses certain features of atomic structure which are changeable. Excellent experiments in this respect have been carried out by Laubengayer and co-workers (9).

The very small atomic size and the large charge of its simple ions give it a tendency for covalent nonmetallic behavior. Ammonia and boron fluoride combine to form the compound $H_3N:BF_3$, in which the nitrogen donates its electrons to the boron. The interesting experiments of Laubengayer and co-workers have demonstrated the activation or excitement of oxygen and boron in experiments with etherates of boron. In the following equation:

$$\begin{array}{c} CH_3 \\ \diagdown \\ O \; + \; BF_3 \; \longrightarrow \\ \diagup \\ CH_3 \end{array} \qquad \begin{array}{c} CH_3 \quad\; F \\ \diagdown^{a} \quad | \\ O-B-F \\ \diagup \quad | \, b \\ CH_3 \quad\; F \end{array}$$
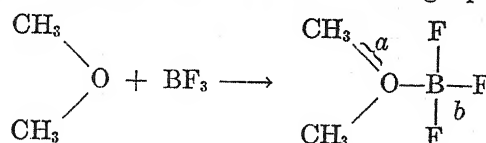
$BF_3$, which has a plane structure, changes to an arrangement in which the boron valence angles are tetrahedral. As a result, the bond distance $b$ becomes enlarged and also, but somewhat less, the bond distance $a$. The bonds of the original molecules are thus weakened, and at the same time the donor may be considered as losing some interest in a part of electrons and so acquires a positive charge, while the acceptor acquires a negative charge.

The shifting of electrons of combining atoms may lead also to the formation of radicals or free atoms which are themselves very reactive and in which we are mainly interested in this article. Radicals are compounds the electronic structure of which possesses a nonsaturated spin moment. In this short paper we have to limit ourselves to two trace elements, iron and copper, in an endeavor to remain on solid ground of sound experimental research. With these two elements, most remarkable discoveries have been made in recent years concerning the mechanism of inorganic components in enzyme systems, and our problem is a part of enzyme chemistry. The results obtained with iron and copper concerning the elucidation of the mechanism of trace metal action have, of course, a bearing on other trace elements, particularly those elements which belong to the transition groups.

### SIGNIFICANCE OF MAGNETOCHEMISTRY IN THE ENZYMATIC SYSTEM

There are many enzymes which consist of some inorganic component such as a metallic ion to which a protein is attached. Sometimes the metallic ion is the central atom of a ring structure or is boxed in an organic structure of nonprotein character (fig. 2). The latter compound is sometimes referred to as a coenzyme or a prosthetic group. Chlorophyll and hemoglobin belong to this class, where a sixteen-membered organic ring structure, porphin (fig. 3), forms the box. In this article we are chiefly interested in ascertaining why nature uses trace metals in cooperation with proteins and how the protein is attached to the metal.

Both iron and copper, from the point of view of genetic considerations, seem to be of vital importance in a great number of basic life processes like respiration and other vital functions of the living matter.   It is of interest that copper as a bio-
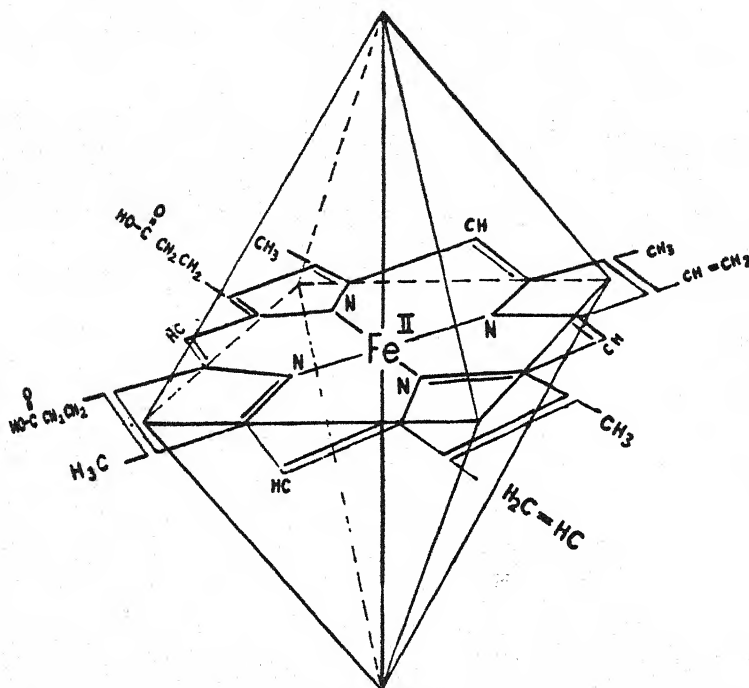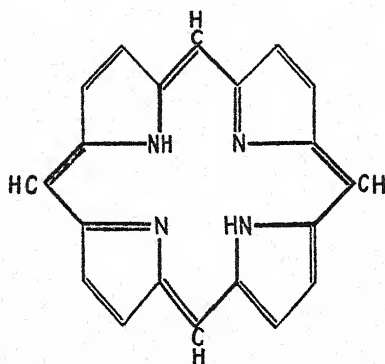


FIG. 2. RED BLOOD PIGMENT



FIG. 3. PORPHIN

catalyst in many enzymatic systems (ascorbic acid oxidase, polyphenol oxidase, laccase, hemocyanin, and others) is directly attached to nitrogen atoms of the protein molecule.   In such a combination it should perhaps not be too difficult to find out the mechanism of the enzymatic system, because we avoid here the

complicating ring structure of the prosthetic group. The fact is, however, that the first ferment in which the nature of the prosthetic group was discovered was the respiration ferment of Warburg. Iron, so far as we know at present, is always protected in a porphin ring structure, as in hemin or other heme compounds. Porphin derivatives with side chains in the $\beta$-position are called "porphyrins." Research on the heme, or iron, or porphyrin compounds during recent years has given us a deep insight into the mechanism of such enzymatic systems. For instance, hemoglobin is a conjugated protein containing native globin and a complex constructed of an iron central atom inserted in a porphyrin. The magnetic moment in ferrohemoglobin (ferroheme plus globin—there are four hemes per globin molecule) is about 4.91 just like an iron ion ($Fe^{++}$) in an ordinary inorganic iron salt. On the other hand, oxyhemoglobin and carbon monoxide hemoglobin have zero moments. The magnetic measurements in the heme compounds reveal important facts concerning the bonding of the iron to protein molecules. The organic porphyrin framework, which nature has provided, has a paramount purpose, namely, to control the electronic configuration of the central iron ion.

In the last analysis, all the combinations of trace elements, especially of the transition group, are Werner complexes. These are chemical compounds which consist of a center atom or positive ion surrounded by neutral or negative atoms or groups of atoms. The example of the heme-compounds shows clearly that Werner's coordination system is the key to the understanding of the function of metallic ions in physiological processes.

More than 20 years ago Welo and the writer started research in an attempt to interpret magnetic susceptibilities in terms of chemical structure. Welo has measured hundreds of metal complex compounds magnetically. As a result, the Welo and Baudisch rule was expressed thus (11): "The magnetic moment of a complex is the same as that of the atom with the same number of electrons as the central atom of the complex, counting two for each pair." This rule still holds well despite exceptions. In spite of the fact that 20 years ago we tried to correlate our results directly with biochemical problems, our magnetochemical research did not arouse much attention among biochemists because the electron theory of valence was still in its infancy and foreign to most biochemists. How different it is today. In the last few years magnetic susceptibility has taken its place, along with dielectric constant, electron diffraction, x-ray diffraction, and molecular and atomic spectra, as one of the most powerful tools at the disposal of the chemist (11). From all this, it is to be seen that magnetochemistry leads to elucidation of changes and reactions in subatomic realms, and now we use this new tool in trace metal research with great success.

The writer has discussed in former papers the question as to how the chemical and physiological behavior of elements is correlated with the formation of Werner complexes, which in turn depend on their atomic or electronic structure. There is an apparent generalization, namely, that atoms and their simple ions tend to gain electrons by coordinating atoms or groups of atoms and thereby to approach the completion of a stable electronic configuration (rare-gas configura-

tion). First of all, the transition elements have a strong tendency to accept or absorb electrons. The molecular dimensions or the size of the radii of atoms is also of importance, since the number of atoms or groups of atoms which can surround another acting as a central atom or nucleus is, of course, limited. Also the size of the addenda or coordinated atoms has a definite influence. Of vital importance in understanding the function of the trace elements is a knowledge of the bond type between the central atom and the attached groupings. For clarity, the names and symbols which are conventional in explaining the bondings, for instance between M and S, are listed, as follows:

$$\text{Electrovalence } M \cdot + S \rightarrow M^+[S^-]$$
$$\text{Covalence} \qquad M \cdot + \cdot S \rightarrow M{:}S$$
$$\text{Donor-acceptor valence } M{:} + S \rightarrow M{:}S$$
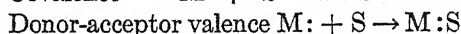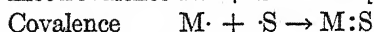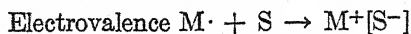
From the bond type the magnetic properties of the central metal atom can be deduced, and *vice versa*. Of equal importance are the characteristics and structure of the organic groupings which are attached with the trace metal. This fact has been excellently demonstrated in the heme compounds by the attached protein molecules of different structure. The protein constituents primarily determine the specificity of the enzyme; the prosthetic group is less specific.

The question is now: Can we demonstrate that a metallic ion (as such, or boxed in) by combining with a protein molecule changes the electronic structure of the metal as well as the chemical and spatial structure of the attached protein? It is known by experience that the number and arrangement of electrons in a metal determine the characteristic mode of bonding of the metal with other atoms, molecules, or groups. The changes which take place in this respect by combining the metal with nitrogen-containing compounds are best expressed in the interrelationships between the various derivatives of iron protoporphyrin. These derivatives (10) are shown in figure 4.

Since in hemochromogen compounds, the maximum coordination number of the iron (six) is reached, oxygen can be attached to the metal only by displacing a nitrogen atom:

$$\text{:Fe:O:O:N}$$
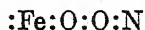
Welo and the writer showed 20 years ago that oxidation of this type takes place when iron acts as a specific catalyst in the oxidation of nitrogen-containing compounds of biological importance. There is no better example in enzyme chemistry than the research on heme compounds which reveals the importance of nitrogen atoms attached to iron. On account of the attachment of the pyrrol-ring structure of globin, pyridine, nicotine, or dicyanides, the resulting iron-containing Werner complexes become endowed with valuable properties and characteristics vital to the life of the cell. These compounds are indeed a model to demonstrate the mechanism of the action of a trace metal in a prosthetic group (coenzymes of oxidation enzymes). They demonstrate that the electrons, which are the "organs', by means of which the atom makes contact with its environment, become more easily available in a structurally defined system. An example will elucidate this statement more clearly.

Hemin (fig. 5) has been found in living plant and animal cells by spectrographic means. Its iron atom exhibits the complete paramagnetism of inorganic iron ions and also their complete electron shell. It easily adds one electron and
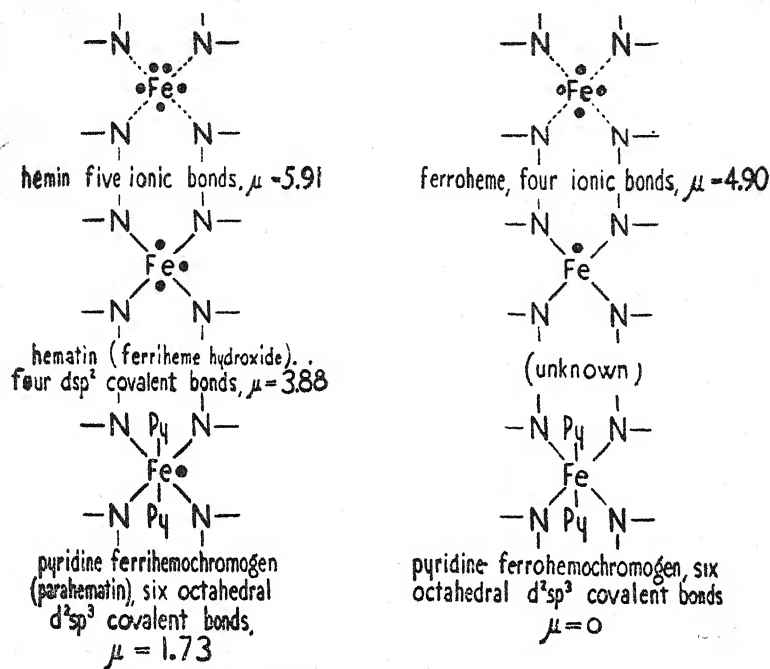


hemin  five ionic bonds, $\mu$ ~5.91

ferroheme, four ionic bonds, $\mu$ ~4.90

hematin (ferriheme hydroxide).
four $dsp^2$ covalent bonds, $\mu = 3.88$

(unknown)

pyridine ferrihemochromogen
(parahematin), six octahedral
$d^2sp^3$ covalent bonds,
$\mu = 1.73$

pyridine ferrohemochromogen, six
octahedral $d^2sp^3$ covalent bonds
$\mu = 0$

FIG. 4. DERIVATIVES OF IRON PROTOPORPHYRIN
The black dots indicate Bohr magnetons or micromagnets.
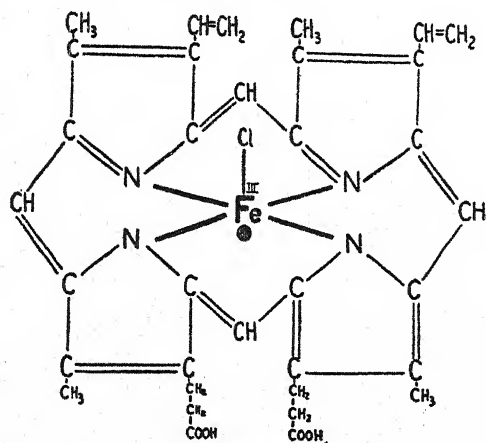


FIG. 5. HEMIN

is thus suitable for intermediate catalysts. Hemin has also a strong catalytic action. The addition of protein, as in catalase, however, increases this catalytic action enormously, and we may assume that the polypeptide structure, after

being "excited" by the bonding to iron is now able to transfer electronic energy. We can be certain that in the groups of the oxidation ferments only an "electronic" mechanism comes into consideration.

### THE PROTEIN COMPONENT OF ENZYMES

We have so far discussed only the electronic structure of the central metallic atom or ion and have said nothing about changes which must take place in the nitrogen atoms of the various addenda. It is obvious that the most important, but at the same time most perplexing, question in enzyme chemistry is protein structure and protein attachment to the coenzyme. We are here interested only in such cases where the prosthetic group (coenzyme) is a metallic ion. As we have said before, copper ions serve as a coenzyme. Then we must assume that nitrogen of the protein is linked to copper. After combination has taken place,
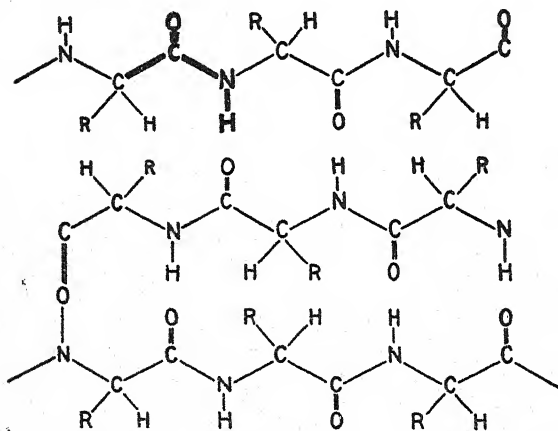


FIG. 6. COPPER PEPTIDE COMPLEX

the nitrogen atoms of the polypeptide chains are probably in an "excited" stage and become very reactive. Even if only *one* atom of copper combines with one nitrogen atom of the attached protein and converts this diamagnetic nitrogen into a paramagnetic one, thousands of nitrogen atoms of the crystal-like polypeptide chain structure may be affected and become somewhat activated. These polypeptide chains are now able to transfer wandering electrons and use them where they are of greatest need (figs. 6, 7, 8).

From the foregoing it can be seen that the central iron ion in oxidation ferments is surrounded by nitrogen atoms. In the hemochromogens there are six nitrogen atoms, of which four are donated by the pyrrol structure and two by protein or other nitrogen-containing components. Thus all the incomplete shells of the iron atom or ion are filled out by the donation of electrons from the surrounding nitrogen atoms. In spite of the fact that such compounds are diamagnetic, strongly paramagnetic molecules like $O_2$ or NO are able to replace one nitrogen atom as we demonstrated before, or go between the metal and the nitrogen.

It is of great significance to biochemical reactions that paramagnetic atoms or groups of atoms are able to unite with diamagnetic or very feebly paramagnetic compounds. The paramagnetic gases like $O_2$ or NO are able to induce magnetism in the other compounds by changing their electronic structure (electronic isomerism). As a result of this change, the compounds become endowed with "metallic" behavior. If radical formations takes place, the compounds become even
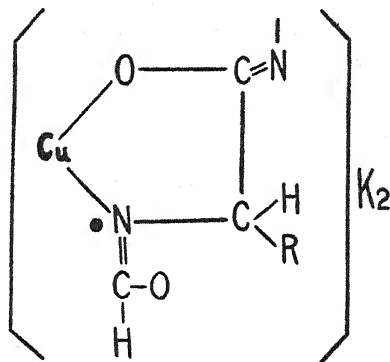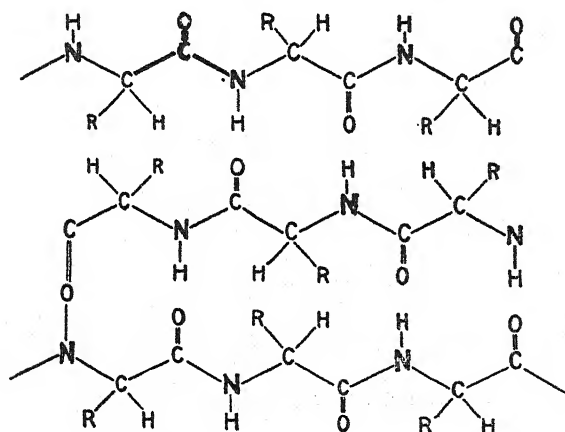


Fig. 7. Structure of Protein



EXCITED NITROGEN ATOMS

Fig. 8. Structure of Protein

strongly paramagnetic. In this way carbon compounds become ions, and purely organic compounds become magnets.

In nature the ethylene linkage is of tremendous importance. Inserted ethylene linkages are paramagnetic or can become so by electronic arrangement if paramagnetic bodies become attached to them (fig. 9). The paramagnetic form, which possesses free spinning electrons, or micromagnets, is able to link other magnetic compounds by sharing electrons or compensating the spin. If we can demonstrate that a metallic ion can convert a feebly reactive diamagnetic organic compound like protein into a paramagnetic compound of extreme reac-

tivity, we may have found the key to an understanding of the biological import-
ance of trace elements. The writer believes that in biological processes the
formation of paramagnetic fields brought about by the bonding of trace elements,
atoms, or groups of atoms is of paramount importance. The reversible formation
of diamagnetic and paramagnetic conditions, diamagnetic $\rightleftarrows$ paramagnetic, in
biological systems has not been sufficiently studied. The experimental diffi-
culties are very great and the methods for measuring magnetic susceptibilities
are not yet sensitive enough for finding extremely short-lived radicals during a
chemical reaction. In respiration and in the reduction of quinones, free radical
formation has been demonstrated. The discovery of biradicals, to which the
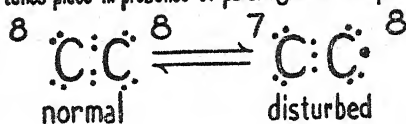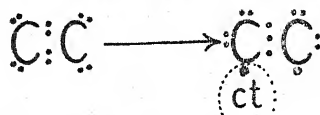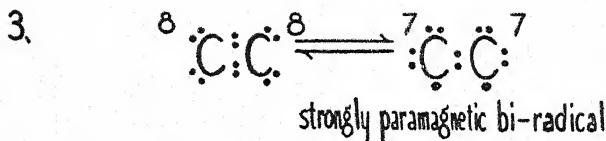


FIG. 9. ELECTRON SHIFT IN ETHYLENE LINKAGES

oxygen molecule belongs, is most important. The identification of bond types
and the determination of space configurations in the complex ions are of extreme
value in the understanding of the biological action of trace elements.

To study the enzymes which use the copper atom or ion as the prosthetic
group is of special interest. We know much about the electronic structure of
copper. It is, however, still a most difficult problem, since the structure of the
protein is unknown. We must, therefore, study first the changes which take
place in a simple nitrogen-containing compound like nitric oxide, NO, after the
NO molecule has bonded itself to copper. For this investigation we have to
find a chemical reaction *in vitro* in which copper is unique, as in the polyphenol
oxidases. The writer has found such a reaction (*B* reaction, for short). If, in

nitrosyl NOH, the hydrogen is replaced by monovalent copper, the resulting compound $Cu^INO$ is a water- and organic-solvent-soluble radical of great reactivity. In the compound $Cu^INO$ the nitrogen contains the free spinning electron, since the nitrogen reacts easily at room temperature with aromatic hydrocarbons like benzene and toluene and forms an intermediate autoxidizable compound. The resulting o-nitrosophenol compounds form a deep red compound with cupric ions and thus can be isolated easily. In the case of benzene in regard to the mechanism of the B reaction, the scheme shown in figure 10 is suggested.

The B reaction takes place in acid solution. In the reaction system free radicals like CuNO, NOH, NO, and H may be expected and may form members of a long chain (chain reaction). Thus one atom or ion of copper may bring about the conversion of thousands of molecules of benzene into o-nitrosophenol.
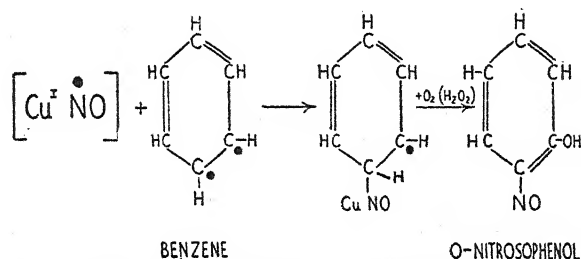


BENZENE                    O-NITROSOPHENOL

FIG. 10. MAGNETIC COUPLING OF NITROGEN WITH CARBON

The copper acts as a catalyst. In the B reaction, copper also stabilizes the short-lived radical NOH and makes it a metallic radical with the free spin on the nitrogen. The NO is extremely loosely bound to the copper, and in the complex $Cu(NO)Cl_2$, NO can be driven out by $CO_2$ gas (1). It is to be assumed that certain metals linked to polypeptides bring about a rearrangement in the nitrogen atoms similar to the one we have found in the B reaction. The copper ion $Cu^I$ with its feeble paramagnetism links the NO molecule or it reacts with polypeptides in the way suggested by Küntzel and Dröscher (8) as shown in figure 6.

The attached trace metal, in our special case copper, brings about a molecular arrangement of the polypeptide structure and in general activates the protein.

In the formula $Cu^INO$, the nitrogen atoms become magnets on account of uncompensated electrons and so acquire radical character. In such cases we speak of resonance or electroisomerism. The enzyme action possibly occurs in a manner parallel to the formation of the stabilized free radical brought about by the donor-acceptor binding of copper ions. In this action we must seek the foremost value and importance of trace elements of the transition groups. The large magnetic susceptibility of the transition metals is considered on good evidence to arise from the electron valencies in the M shell, for the magnetic susceptibility diminishes if electrons are added to the d band (d orbital in M shell).

The relation of electron configuration, magnetic susceptibility, and trace elements as outlined in this short article is undoubtedly more complicated in many respects. But the existence of simple and fundamental relations between the central atom and the added atoms or groups of atoms and their significance to magnetochemistry suggests the possibility of a new approach to the general problem.

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# USE OF MICROORGANISMS TO DETERMINE ESSENTIALITY OF MINOR ELEMENTS

ROBERT A. STEINBERG

*U. S. Department of Agriculture*

Minor element studies with fungi[1] antedate those with other organisms. Fungi also were first used for vitamin and antibiotic compound (penicillin) studies. Major advances in these fields had their inception in the studies of soil fungi—*Aspergillus*, *Penicillium*, *Phycomyces*, and *Saccharomyces*. This can be attributed in part to the accuracy, speed, and precision with which these organisms can be grown under semimicroscale conditions of rigid experimental control. Little advantage has yet been taken, however, of the possibilities for research inherent in these forms because of their widely different requirements and responses to alterations in their diet. This is true depite the economic importance of their activities in nature.

Work on minor elements with microorganisms has been largely confined in recent times to that with *Aspergillus niger* and to studies by the writer (3). These have aided in correcting the view of many that growth increases with trace elements were phenomena of toxicity, *i.e.*, "chemical stimulation." They have led to the introduction of the calcium carbonate method for removal of minor elements from nutrient and culture solutions. Verification was obtained of Raulin's (1869) findings that iron and zinc are essential, of Bertrand and Javillier's (1911) respecting manganese, and of Bortel's (1927) concerning copper. Proof that molybdenum (1936) and probably gallium (1938) are indispensable for growth was also obtained with this organism. Dietary studies have, therefore, revealed that at least five or six of the minor elements are micronutrients for *Aspergillus niger*. It must be admitted, however, that full concurrence of others as to their general role awaited discovery of the functions of copper and manganese in hemoglobin formation, and of manganese (McHargue), boron (Warington), and zinc (Hoagland *et al.*) in deficiency diseases of crop plants.

## DIETARY REQUIREMENTS OF A. NIGER

The basis for the successful use of *A. niger* as a test organism for minor element studies is a knowledge of its fundamental nutritional requirements. As a result of successive studies, the quantity of macronutrients found to be required has decreased progressively from 17.5 gm. per liter to 2.5 gm., while micronutrients increased from a "trace" of iron to 1.04 p.p.m. of Fe, Zn, Cu, Mn, Mo, and Ga. With 50 gm. of sucrose per liter the yield is $20 \times 1.25$ gm. per liter (dry weight) in 4 days at 35° C. with an inoculum of 250 $\gamma$: an increase of 1:100,000 in mass. Other required macronutrients are nitrogen, potassium, phosphorus, magnesium, and sulfur. Sodium, chlorine, silicon, and calcium do not seem necessary, nor do boron, iodine, and cobalt.

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[1] Much important work along similar lines has been done with soil bacteria (Azotobacter, Rhizobium). Space does not permit of its discussion.

This "optimum solution of minimum salt content" for maximum normal growth has been pointed out to possess physiological specificity (4). It represents the specific minimum requirements of the fungus for the chemical elements under the experimental conditions employed. This solution or diet will be termed "dibasal" hereafter. It corresponds to the "balanced" animal diet of H. H. Mitchell (1934).

The proportions of the elements in the dibasal solution are fixed though probably dependent somewhat on the stage of growth reached. These proportions do not alter with a variation in quantity of energy supply (sucrose) over a 1 to 3 range. Total quantity of this salt mixture required is directly proportional over the same range to the quantity of energy supplied. It is evident, therefore, that *the dibasal requirement for each element by the fungus is directly proportional to the quantity of carbohydrate available for growth.* Exactly reproducible quantitative results in nutrition are possible, moreover, only with a fixed carbon supply.

Absorption of the dietary constituents of the dibasal solution approaches 100 per cent[2] and does not alter appreciably over a threefold variation in total concentration. Total ash in the fungus and its composition are similarly invariant over the same concentration range. It is clear from these results that total and relative quantities are the important factors in dietary studies and not concentration. The latter must be viewed as a purely physical environmental factor like temperature and humidity and may usually be disregarded except for avoidance of extremes.

*Aspergillus* can absorb far greater quantities of dietary and nondietary constituents than is possible with the dibasal solution. Accumulation of unusual (actually unnecessary and useless) quantities of specific elements by this fungus, as with "accumulator plants," is usually regarded as an example of marked selectivity in absorption. The opposite view would seem more logical to the writer, namely, that accumulation follows because of poor selectivity in absorption, a high degree of tolerance, and a high saturation or storage capacity. Plants vary widely in composition of ash with variation in their substrata, not because they have no specific requirements but because of imperfect selectivity in absorption. An organism possessing perfect selectivity in absorption should absorb only such substances, qualitatively and quantitatively, as would meet its specific requirements regardless of variable substratum or diet. Additional support for this view is given by the rigid specificity in requirements of *A. niger* per unit of normal mass formed in a dibasal solution, where exercise of the plant's selectivity in absorption is prevented.

There is no conflict between this interpretation and the data of ion absorption. One deals primarily with internal limiting factors and the other with the mechanism whereby absorption is accomplished. Internal factors might, of course, possibly influence rate of absorption in some instances ("low-salt" barley roots). Absorption, however, is not a passive process but is associated with a respiratory expenditure of energy in sugar (1) employed perhaps in the process of amino

[2] Unpublished data.

acid and protein formation. This series of reactions in its entirety is probably identical with "metabolism," in view of the evidence of Vickery and his associates (1940) that amino acids in proteins undergo continual breakdown and replacement by new and probably freshly synthesized units.

### CRITERIA FOR BIOLOGICAL ESSENTIALITY

The criteria for essentiality during the course of the writer's studies have also undergone a gradual evolution and clarification. Proof of an indispensable nutritive function of a chemical element is now considered as afforded only through nutritional experimentation. Positive results imply that *the diet is proportioned and just adequate (dibasal diet) for maximum normal growth* if the element is added, and unsatisfactory if omitted, and that *other elements of similar chemical properties cannot be so employed.* Collateral data are important only insofar as they aid or substantiate.

*In vitro* enzymatic reactions may be different from those in the organism under normal checks and accelerations. Frequently several elements may serve to activate an enzyme. It is fallacious to assume that the organism must employ the most efficient of these in its nutrition. Overall efficiency in all its reactions, rather than specific individual efficiencies, is probably the basis for nutritive essentiality and specificity in the organism. Even the formation of characteristic metabolites of an element may be immaterial as proof, if the organism is capable of dispensing with it (*e.g.*, chlorine in fungi).

A brief word should be added with regard to biological specificity as a criterion for essentiality. All nutritive elements possess biological specificity. Nevertheless, biological specificity is not full proof of biological essentiality. A single illustration will make this clear. Sodium can replace potassium to some degree in the nutrition of some green plants, but lithium, rubidium, and cesium cannot. Unpublished data of the writer reveal that *Aspergillus* responds similarly. This specific biological response to sodium is no proof of its essentiality to either green plant or fungus, since either can apparently dispense with its presence.

A nutritive chemical element therefore is one whose omission from a dibasal diet results in decreased growth, morphological abnormality, and/or death of the organism according to the degree of deficiency. Yield, in itself, has frequently proved to be a poor criterion for essentiality, because of an inadequate study of the diet as a whole.

### DEFICIENCY SYMPTOMS

Deficiencies in micronutrients, as with macronutrients, are in all cases reflected by a diminution in yield and, if the deficiency is sufficiently extreme, by morphological abnormalities. With present levels of experimental purity, losses in yield with deficiency approach the following percentage values with *Aspergillus*: N, 100; K, 94; P, 100; S, 98; Mg, 100; Fe, 100; Zn, 100; Cu, 65; Mn, 82; Mo. 96; Ga, 62. The conclusion is inescapable, therefore, that the few parts per million or billion of the micronutrients are as important to the fungus as are the far larger quantities of macronutrients it also requires.

Comment is necessary on these values in two instances. The result for potassium was obtained in the presence of sodium, whereas that with gallium is no longer reproducible to the same degree. Decreased responses on omission of gallium from the solution were concomitant with exhaustion of a special supply of sucrose. Other samples of sucrose obtained subsequently gave poorer results than the original sample. Special techniques developed for removal of minor element impurities from sucrose have also proved ineffective so far with gallium, though sufficing otherwise to give results equivalent to calcium carbonate purification. An interesting fact in this connection is that sucrose purification followed by calcium carbonate (actually CaO was used) purification is more effective than the latter process alone. It should be recalled, however, that the quantity of gallium required is not over 20 parts per billion.

Morphological abnormalities accompany extreme deficiencies in nutrient elements in *Aspergillus*. Absence of extensive morphological differentiation does not permit of the degree of specificity in symptoms shown by most green plants. In all instances sporulation is decreased or suppressed, and in the case of copper deficiency spore color progressively decreases from black to brown, tan, yellow, and white. Moreover, the reverse of the fungus, where it is in contact with the solution, becomes distinctly pink when copper is insufficient. Even slight deficiencies in copper and manganese are reflected in decreased spore formation. Minus-molybdenum cultures on $NH_4NO_3$ are decidedly flaccid. Deficiencies in N, P, S, Mg, Fe, Zn, and Mo result in marked retardation of polysaccharide formation, *i.e.*, the cell walls become thin and translucent. Deficiencies in K, Cu, Mn, and Ga do not give this response. Manganese deficiency is particularly striking—the many tiny individual colonies floating on the solution are very white and hard to the touch. A drop of 0.05 $N$ iodine gives an immediate brilliant blue coloration similar to that given by starch: chitin seems to be absent.

### FUNCTIONS OF MOLYBDENUM

The writer has studied the effects of varying dietary components on the micronutrient requirements of *A. niger*. Variations in composition of carbon, nitrogen, and sulfur supplies were immaterial in affecting responses to micronutrient deficiencies except that of molybdenum. Molybdenum deficiency resulted in losses in yield of 96 per cent with nitrate-nitrogen, and perhaps 4 per cent with ammonium-nitrogen. With ammonium nitrate the loss in yield was about 45 per cent.

The beneficial biological action of molybdenum was first reported by Bortel (1930) for *Azotobacter* and *Rhizobium* and was considered by him to hold only in the utilization of atmospheric nitrogen. Vanadium could partially replace molybdenum.[3] These results were verified and amplified by Burk and co-workers (2) with *Azotobacter* in a series of thorough studies. Discovery of its necessity for *Aspergillus niger* revealed the real function of molybdenum to be that of a micronutrient.

[3] Bertrand (1941) considers vanadium a micronutrient for *A. niger*.

The specific biochemical functions of molybdenum in microorganisms are not yet clear. The importance of its addition is greatest for *Aspergillus* with nitrate-nitrogen and decreases proportionately with substitution of ammonium-nitrogen. Molybdenum is also required with nitrite-nitrogen, and with nitrogen as nitro-hydroxylaminic acid. Only when reduction of nitrate has proceeded as far as hydroxylamine does the need for molybdenum seem to diminish. Deficiency in molybdenum is accentuated by growth of the fungus in $CO_2$-free air. Taken in conjunction with results on fixation of atmospheric nitrogen by bacteria, these data would indicate a close relation between the biochemistry of nitrogen utilization and molybdenum. The decreased molybdenum requirement on substitution of nitrogen salts for gaseous nitrogen with *Azotobacter* and of ammonium for nitrate with *Aspergillus* may have a common basic significance.

Molybdenum is the most recent of the trace elements definitely demonstrated to be a micronutrient for plants. The writer's experience, therefore, may be helpful to others. Using triply distilled water (building steam condensed in pyrex, and twice redistilled in quartz) and selected reagent chemicals, one should have no difficulty in obtaining deficiency losses of 96 per cent with *Aspergillus* and 80 per cent with *Lemna*. Redistillation of water is unnecessary for results on molybdenum except in most exacting work. In *Lemna* the fronds adhere into rosette-like clumps with long green twisted roots. Fronds become unevenly light green merging into white, and their apexes become acute and turn upward. These symptoms are quite distinct from those of iron, manganese, and boron deficiencies.

## CONCLUSIONS

The mineral requirements of *Aspergillus niger* agree with those of the green plant except for calcium, silicon, and boron, though other fungi may be found to require calcium, silicon, and boron. It can therefore be used as a test organism when accuracy, speed, and precision are necessary; or when aseptic conditions or those of extreme purity are required. Comparative studies of its requirements and metabolism with those of other fungi and green plants should aid in revealing the biological functions of the chemical elements in plants.

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# STUDIES ON THE LIFE CYCLE OF VETCH NODULE BACTERIA

## H. ZANYIN GAW

*National Wuhan University, Kiating, Szechuen, China*

The pleomorphic nature of root nodule bacteria was the subject of many controversies among the early investigators, and many theories as to the nature and function of the different forms were advanced. The early studies on the subject have been reviewed by Fred, Baldwin, and McCoy (2), and more recent works, by Lewis (3).

This investigation was undertaken to find out whether the vetch nodule bacteria undergo morphological changes in different culture media and in soil and pass through the stages described by other workers. A study of morphological variations is important insofar as it may serve as a clue to the physiological behavior of the organism.

## LIFE CYCLE IN CULTURE MEDIA

### Experimental materials and methods

The morphological changes of vetch nodule bacteria (V103, V104, V106) cultivated in a variety of media and stained with various dyes during the growth cycle were studied. The media used were nitrate mannitol agar, vetch extract, soil glucose agar, beef peptone glucose, and nutrient agar. The stains used were gentian violet, methylene blue, Barrow's stain, carbol thionin, and carbol fuchsin.

Microscopic examinations were made of cells from young and old cultures, ranging in age from 24 hours to more than 24 days.

### Results

Observations made during the course of this investigation indicate that the vetch nodule bacteria do not pass through a complicated life cycle, as described by previous workers, particularly Bewley and Hutchinson (1). When cultivated on different media, however, these bacteria present different morphological forms. In nitrate mannitol agar and soil glucose agar, the cells from young cultures are mostly cocci and short rods, whereas in cultures 4 or more days old, rods as well as branched forms are observed, and banded or vacuolated cells are not uncommon. Previous writers have paid special attention to these vacuolated cells because they were considered to be the bearers of gonidia. Though the more or less spherical granules inside the cells do resemble these reproductive bodies, especially when cocci are also present, there is no positive evidence that these bodies are released from the vacuolated cells to become cocci. Lewis (3) presented a critical discussion of this point and concluded that these bodies are cell-inclusions of fat-like substance bearing no relation to reproduction. Previous conceptions of them as bearers of gonidia are based on erroneous interpretations

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of the cell structure. In vetch extract medium, there is scarcely any change in morphology. Rod forms are predominant from very young cultures to old ones. In this medium, branched forms and vacuolated cells are not seen. In nutrient agar and beef peptone agar, the cells are cocci and very few rods. No branched forms are seen, although in the latter medium, vacuolated cells are common.

According to Lewis (3), the principal factor that favors formation of fat bodies is the composition of the culture medium. They are more abundant in media containing mannitol, glucose, or sucrose. On the other hand, Bewley and Hutchinson (1) claimed that the formation of banded cells depends on the absence of carbohydrates. Such cells are more abundant in soil extract without carbohydrates and do not occur in carbohydrate media. The present results agree with the view of Lewis as these bodies are observed in carbohydrate media; namely, nitrate manitol, soil glucose, and beef peptone glucose.

In general, the results of the present work agree with the observations and conclusions of Lewis. The growth phase of vetch nodule bacteria reveals nothing unusual. Although morphological variations are exhibited in the cultures observed, such changes in no sense represent stages in the bacterial life cycle.

As pointed out by Lewis (3), when cells from old cultures are transplanted to fresh media and examined during the early and late phases of growth, an orderly sequence in development occurs. Such changes are not due to a cyclogenic life history. The term "growth cycle" is therefore suggested, indicating a repetitive sequence in the growth phases of cultures when transplanted at appropriate intervals. There is, of course, no reason to doubt that these transitions are influenced by culture media and other conditions of cultivation.

## LIFE CYCLE IN SOIL

### Experimental materials and methods

To avoid confusion in interpreting results, the method of studying the life cycle of nodule bacteria in soil adopted by Thornton and Gangulee (4), with a few minor changes, was followed in this experiment. Petri dishes 4.5 inches in diameter containing about 150 gm. of a mixture of 40 per cent Kiating loam and 60 per cent sand were used. The water content was made up to about 40 per cent on an air-dry basis. The culture used was V105 of our laboratory collection, the purity of which was tested before the experiment.

Sampling was made each time with sterile glass tubing from four different parts of the Petri dish at hourly intervals for the first 12 hours and then daily for 6 days. The film was air-dried, fixed in absolute alcohol, and stained with phenol erythrosine stains as recommended by Thornton and Gangulee. As these stains did not prove to be very satisfactory, other stains such as methylene blue and carbol thionin were also used. Three cultures were followed with triplicate preparations made from each culture. The percentages of cocci, banded rods, and unbanded rods were determined for each slide according to the method of Thornton and Gangulee.

## TABLE 1

*Unbanded rods, banded rods, and cocci found in soil culture A*

| TIME OF OBSERVATION | TOTAL NUMBER OF CELLS COUNTED | UNBANDED RODS | | BANDED RODS | | COCCI | |
|---|---|---|---|---|---|---|---|
| *hours* | | *number* | *per cent* | *number* | *per cent* | *number* | *per cent* |
| 1 | 156 | 124 | 79.5 | 32 | 20.5 | 0 | 0 |
| 2 | 135 | 98 | 72.5 | 18 | 13.3 | 19 | 14.2 |
| 3 | 182 | 116 | 63.8 | 43 | 23.6 | 23 | 12.6 |
| 4 | 251 | 203 | 80.8 | 34 | 13.5 | 14 | 5.7 |
| 5 | 128 | 79 | 61.7 | 43 | 33.5 | 6 | 4.8 |
| 6 | 104 | 62 | 59.6 | 11 | 10.5 | 31 | 29.9 |
| 7 | 342 | 241 | 70.6 | 92 | 26.8 | 9 | 2.6 |
| 8 | 310 | 225 | 72.6 | 67 | 21.6 | 18 | 5.8 |
| 9 | 155 | 113 | 73.1 | 18 | 11.5 | 24 | 15.4 |
| 10 | 93 | 84 | 90.4 | 9 | 9.6 | 0 | 0 |
| 11 | 303 | 130 | 43.0 | 101 | 33.3 | 72 | 23.7 |
| 12 | 133 | 43 | 32.3 | 56 | 42.2 | 34 | 25.5 |
| 24 | 89 | 52 | 58.6 | 21 | 23.5 | 16 | 17.9 |
| 48 | 166 | 117 | 70.4 | 29 | 17.6 | 20 | 12.0 |
| 72 | 244 | 209 | 85.6 | 16 | 6.5 | 19 | 7.9 |
| 96 | 188 | 142 | 75.5 | 38 | 20.3 | 8 | 4.2 |
| 120 | 149 | 83 | 55.7 | 42 | 28.2 | 24 | 16.1 |
| 144 | 160 | 109 | 68.1 | 20 | 12.4 | 31 | 19.5 |

## TABLE 2

*Unbanded rods, banded rods, and cocci found in soil culture B*

| TIME OF OBSERVATION | TOTAL NUMBER OF CELLS COUNTED | UNBANDED RODS | | BANDED RODS | | COCCI | |
|---|---|---|---|---|---|---|---|
| *hours* | | *number* | *per cent* | *number* | *per cent* | *number* | *per cent* |
| 1 | 205 | 192 | 93.6 | 13 | 6.3 | 0 | 0 |
| 2 | 198 | 174 | 87.8 | 16 | 8.0 | 8 | 4.2 |
| 3 | 355 | 305 | 85.9 | 38 | 10.7 | 12 | 3.4 |
| 4 | 269 | 210 | 77.6 | 43 | 15.9 | 16 | 6.5 |
| 5 | 127 | 94 | 74.0 | 12 | 12.7 | 21 | 13.3 |
| 6 | 202 | 162 | 80.1 | 26 | 12.8 | 14 | 7.1 |
| 7 | 76 | 65 | 85.5 | 8 | 10.6 | 3 | 4.0 |
| 8 | 100 | 89 | 89.0 | 11 | 11.0 | 0 | 0 |
| 9 | 141 | 113 | 80.1 | 21 | 14.8 | 7 | 5.1 |
| 10 | 263 | 212 | 80.6 | 32 | 12.1 | 19 | 7.3 |
| 11 | 181 | 141 | 77.8 | 19 | 10.4 | 21 | 11.8 |
| 12 | 97 | 85 | 87.6 | 0 | 0 | 12 | 12.4 |
| 24 | 136 | 106 | 77.9 | 6 | 4.4 | 24 | 17.7 |
| 48 | 57 | 43 | 75.4 | 14 | 24.6 | 0 | 0 |
| 72 | 132 | 102 | 77.2 | 14 | 10.6 | 16 | 12.2 |
| 96 | 108 | 63 | 58.3 | 27 | 25.0 | 18 | 16.7 |
| 120 | 75 | 54 | 72.0 | 10 | 13.3 | 11 | 14.7 |
| 144 | 115 | 89 | 77.3 | 12 | 10.4 | 14 | 12.3 |

## Results

The results of the experiments are given in tables 1, 2, and 3. Although all the three principal cell types (cocci, unbanded rods, and banded rods) were observed, only the unbanded rods occurred in all the samples examined. According to Thornton and Gangulee (4), the lucerne nodule organisms pass through two complete cycles of changes within the first 27 hours, each commencing with an increase in the production of unbanded rods, followed by a rise in the proportion of cocci and banded rods. The present observations do not substantiate their results. As may be seen from the tables, the proportion of unbanded rods remains higher than 50 per cent almost all the time and there is

### TABLE 3

*Unbanded rods, banded rods, and cocci found in soil culture C*

| TIME OF OBSERVATION | TOTAL NUMBER OF CELLS COUNTED | UNBANDED RODS | | BANDED RODS | | COCCI | |
|---|---|---|---|---|---|---|---|
| hours | | number | per cent | number | per cent | number | per cent |
| 1 | 235 | 217 | 92.4 | 14 | 5.9 | 4 | 1.7 |
| 2 | 239 | 209 | 87.6 | 21 | 8.7 | 9 | 3.7 |
| 3 | 157 | 132 | 84.9 | 9 | 5.0 | 16 | 10.1 |
| 4 | 111 | 76 | 68.5 | 23 | 20.7 | 12 | 10.8 |
| 5 | 119 | 103 | 86.5 | 11 | 9.3 | 5 | 4.2 |
| 6 | 157 | 119 | 75.9 | 21 | 13.3 | 17 | 10.8 |
| 7 | 118 | 63 | 53.4 | 31 | 26.3 | 24 | 20.3 |
| 8 | 254 | 215 | 84.8 | 20 | 7.8 | 19 | 7.4 |
| 9 | 170 | 132 | 77.7 | 17 | 10.0 | 21 | 12.3 |
| 10 | 177 | 97 | 54.9 | 48 | 27.1 | 32 | 18.0 |
| 11 | 163 | 88 | 54.0 | 52 | 31.9 | 23 | 14.1 |
| 12 | 281 | 231 | 82.3 | 32 | 11.3 | 18 | 6.4 |
| 24 | 296 | 169 | 57.2 | 121 | 40.8 | 6 | 2.0 |
| 48 | 235 | 132 | 56.2 | 63 | 26.8 | 40 | 17.0 |
| 72 | 188 | 139 | 74.0 | 19 | 10.1 | 30 | 15.9 |
| 96 | 233 | 84 | 36.0 | 132 | 56.8 | 17 | 7.2 |
| 120 | 223 | 116 | 52.1 | 78 | 34.9 | 29 | 13.0 |
| 144 | 132 | 94 | 71.3 | 24 | 18.1 | 14 | 10.6 |

no regularity of increase or decrease in numbers. On the other hand, except in two instances, banded rods and cocci are not present in proportions higher than 40 per cent, and again, no regularities of increase or decrease in numbers can be observed. The difference between the present observation and that reported by Thornton and Gangulee (4) is difficult to explain, though it may be due to the composition of the soil mixture and to the difference between the organisms.

From our present observations, it may be concluded that the vetch nodule organisms do not pass through regular stages in soil culture, although three morphological cell types were observed. This finding is in agreement with the observations reported in the previous section.

## SUMMARY

Vetch nodule bacteria cultivated in a variety of media as well as in soil do not pass through regular stages. Although morphological variations are exhibited in the cultures observed, such changes in no sense represent stages in the bacterial life cycle.

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# THE FOREST HUMUS LAYERS OF OHIO[1]

LESLIE W. GYSEL

*Ohio State University*

The "humus layer" of forest soils is defined by Heiberg and Chandler (8) as the surface soil which is characterized largely by its organic matter. It has been designated as the $A_0$ horizon[2] below the litter, and in the case of a mull, the $A_1$ horizon. Forest humus, according to Waksman, Tenney, and Stevens (21), is composed of organic residue materials which are undergoing decomposition, constituents of plant products which are less readily decomposed, synthesized microbial cells, and decomposition products of natural materials and cell products.

The importance of the forest humus layers may be determined in part by considering the physical, chemical, and biological effects of humus in the soil. Furthermore, from numerous studies in various sections of the country, it is evident that a large percentage of forest tree roots are in the A horizon. Also roots of many forest shrubs and herbs are entirely in this horizon. Forest humus layers may therefore have important effects upon the growth of forest plants.

Most of the studies of forest soils in the United States have been made in very recent times, mainly within the last decade; therefore many phases of this field, one of which includes the humus layer investigations, have not been adequately studied. The only general sources of information about the characteristics of forest humus layers of Ohio are included in profile descriptions in the Soil Survey Reports of the U. S. Department of Agriculture. Many of the properties of humus layers which might be of value to workers in specialized fields, such as foresters and plant ecologists, are not indicated in most of these descriptions.

The purpose of this investigation is to describe and classify the forest humus layers of Ohio and to designate the relation of these layers to certain environmental factors, mainly topography, mineral soils, and vegetation. In addition, important physical and chemical properties are indicated. A method of classification of the humus layers based on easily recognizable characteristics is utilized. This paper does not present a complete investigation of the subject. It is mainly a reconnaissance which will serve to show in a general way what the forest humus layers are like and where they occur.

## REVIEW OF THE LITERATURE

The early work pertaining to the classification and characteristics of forest humus layers was carried on in Europe, mainly in Denmark, Sweden, and Germany. The most important

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[2] The soil horizon terminology is the same as that used by Kellogg (9).

investigations were those of the Danish worker, P. E. Muller, which were published during the period from 1878 to 1910.   He described the two main humus layer groups, the mull and the mor, which are used as the basis of most classifications at the present time.   In 1931 Romell and Heiberg (16) published the first important classification of the forest humus layers in the United States.   Four years later a more nearly universal classification was presented by Bornebusch and Heiberg (2), and in 1941 a revised nomenclature by Heiberg and Chandler (8), which is primarily for the humus layers of northeastern United States, was proposed as a standard or basis of terminology.   Two main types of forest humus layer—the mull and the mor—were recognized in the region.   The mull type is characterized by a rather thin layer of partly decomposed organic materials which grades gradually into the mineral soil with incorporated organic matter.   In contrast is the mor type, in which
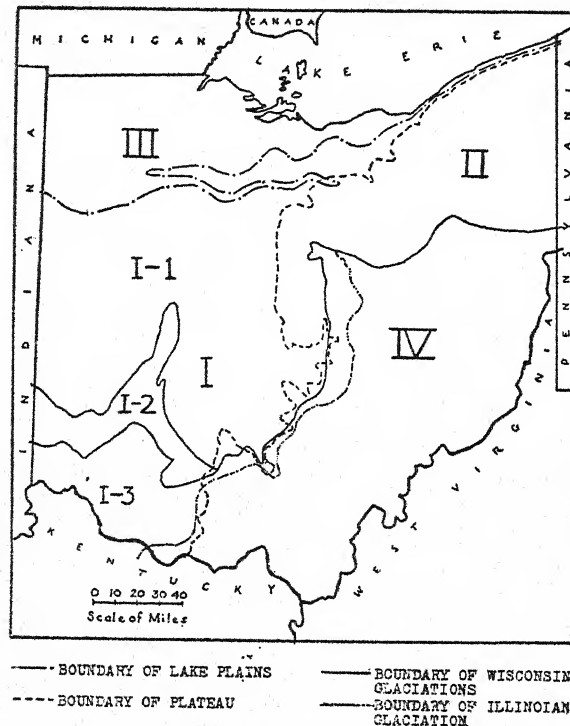


FIG. 1. PHYSIOGRAPHIC PROVINCES AND GLACIATION BOUNDARIES IN OHIO

the demarcation between the decomposing organic matter and the mineral soil is rather sharp, the mineral soil containing relatively little incorporated organic matter.

### PHYSICAL FEATURES OF THE STATE

The following brief description of the physical features of the state forms a general picture of the environmental conditions in which the described humus layers have developed.

### *Geology*

*Topography.*   The state of Ohio can be divided into four physiographic provinces (10) as shown in figure 1: the Till Plains (I), the Glaciated Plateau (II), the Lake Plains (III), and the Unglaciated Plateau (IV).   One of the most marked differences between the

glaciated and the unglaciated sections is in the topography. On the whole, the Till Plains are undulating except in the areas that have morainal hills. The Lake Plains are generally level. In striking contrast to this is the unglaciated or Kanawha section of the Allegheny Plateau which consists of narrow ridges and steep-sided valleys. The glaciated section of the plateau is characterized by rounded hills as well as by wide and shallow valleys.

*Glacial drift.* Evidences of three major glacial advances have been found in Ohio (10). The deposits of the first and oldest, the Illinoian, are visible mainly in the southwestern and east-central part of the state (fig. 1, I-3). The Wisconsin drifts, the Early (I-2) and the Late (I-1), cover most of the glaciated area. During the glaciation there was very little mixing of foreign material with local material, and therefore the deposits are generally like the underlying rock (5). The drift varies from a shallow layer to 500 feet in depth.

*Underlying rocks.* Virtually all of the country west of a line drawn through Sandusky, Columbus, and the eastern part of Adams County is underlain with limestone and calcareous shales. The formations of the eastern half of the state consist mainly of sandstone and shales with some conglomerates (3).

## Soils

*General characteristics.* The gray-brown podzolic soils are the characteristic zonal soils over the entire state (18). They are associated with intrazonal soils, namely, the planosols and half bog soils, mainly on the Till Plains and with azonal soils in the Unglaciated Plateau. Coffey and Rice (5) found that throughout virtually all of the state, soils to a depth of at least 18 inches are low in lime carbonate because of leaching. An exception to this is the dark-colored soils of western and northwestern Ohio, which are usually nearly neutral in reaction. In the western part of the state, a lime carbonate reaction is obtained in the subsoils below 2 feet in depth. The surface and subsoils of the northeastern section of the state are generally acid. Only small areas of entirely sandy soils occur, and the total area of clay is not large. Most of the soils are of medium texture—loams, silt loams, and clay loams.

*Genesis.* Conrey (6) says that leaching has been active in the soils of Ohio and that two zones have developed. Bases and colloidal material have been leached from the uppermost zone, whereas the second zone is one of accumulation in which the fine material has been deposited as well as the precipitates from the leachate.

## Vegetation

*Original forest types.* Before settlement, Ohio was almost entirely forested. The climax association, beech-maple, occurred mainly on the moderately well-drained habitats of the Till Plains, on the Glaciated Plateau, and to some extent in the eastern part of the Unglaciated Plateau. Various communities of the swamp forest were the main vegetation on the flat poorly drained Lake Plains and also on the poorly drained sections of the Till Plains. The southern part of the Unglaciated Plateau was characterized by a number of types which were influenced to a great degree by drainage and exposure. Oak-hickory, oak-chestnut, and oak-hard-pine associations occurred mainly on the south-facing slopes and ridge tops, whereas the beech-maple and mixed mesophytic types were common on the north-facing slopes and in the coves (17).

*Present cover types.* The structure and composition of the primary types have been changed throughout the state. Many of the secondary forests are more poorly stocked than the original stands, and secondary species are often dominant. As a result of the many different kinds of treatment, the cover types which exist now are very numerous, and only those on the areas investigated will be mentioned.

### EXPERIMENTAL PROCEDURE

#### Field observations

*Soil horizons.* The relation of the various humus types to certain environmental conditions was deduced from previous work in other regions and from a

general reconnaissance survey which was made before the final field work was carried out. Fifty-six sample areas were then chosen in all sections of the state to ascertain the general occurrence and properties of each humus type; special emphasis was placed on the selection of plots in areas which were characterized by distinctive environmental conditions. Wherever possible, the soil and vegetation studies were made in undisturbed forest stands. Generally, however, the investigations had to be made in disturbed areas, but with few exceptions, only well-stocked and ungrazed stands were studied.

The study of the surface soil layers was made in the most nearly typical and least disturbed portions of the stands. Numerous test soil pits were excavated for the purpose of determining the general humus type and its variations in each forest area, and one or two of these pits were selected for detailed study.

*Vegetation.* A detailed survey of the vegetation of an area of approximately one-fourth acre was made in each sample woodland. Usually the soil pit was the center of the plot. A list of the tree, shrub, and herbaceous species was made and the density of each recorded. Tree diameters were measured, and notations were made as to the condition and growth. Additional observations were also made throughout the entire woodland area being investigated. From these data, the history of the stand was deduced.

### Laboratory analyses

Laboratory determinations were made only on selected samples, mainly those of the most nearly typical sites. Analyses were made of the $A_1$ horizon or its equivalent for the mull types, of the H layer[3] of the mor types, and of the surface mineral soil layers which are associated with each of the analyzed samples.

*Organic matter content.* The organic carbon content of 37 humus layer samples and of the associated mineral soils was determined by Schollenberger's wet combustion method (1). Because many of the soils were higher in organic carbon than agricultural soils for which the method was primarily designed, smaller samples were used than specified. From 0.05 to 0.2 gm. of air-dry humus layer sample was used with 0.1961 gm. of potassium dichromate when the organic carbon content was below 20 per cent. For samples in which the organic carbon content was over 20 per cent, a 0.05-gm. soil sample with one and one half to two times the specified amount of potassium dichromate was used. The determinations were made in triplicate for the 0.05-gm. samples and in duplicate for all others. The results for each humus type sample generally checked within 2 per cent.

The organic matter content was calculated by multiplying the organic carbon content by the factor 1.724, which is commonly used (20). Lunt (11) has shown that this factor is not accurate for calculating the organic matter content of forest soils, but because separate factors for the calculation of organic matter have not been determined for Ohio soils, it must be used at the present time. The error is not great enough to affect comparative results.

[3] The H layer consists principally of organic matter mostly unrecognizable as to origin.

*Moisture equivalent.* Determinations of the moisture equivalent were made essentially according to the methods suggested by Veimeyer, Oskerkowsky, and Tester (19). The samples were soaked for 96 hours instead of 24 hours in order to assure a more complete hydration of the soils with a high organic matter content. Duplicate determinations were made.

*Acidity.* The pH values of 37 humus layer samples and associated mineral soils were determined by the electrometric method with a glass electrode. Most of the determinations were made on moist samples a short time after collection in the field. The soil-water ratio used was $1:2\frac{1}{2}$ except with soils light in weight per unit volume, with which a 1:7 ratio was used. The mixtures were allowed to stand 24 hours before the determinations were made. Tests of each layer were made in triplicate, and the results generally checked within 0.1 pH.

*Total exchange capacity and exchangeable hydrogen.* A modification of the barium acetate method as described by Chandler (4) was used to determine the total exchange capacity and the exchangeable hydrogen. Sixteen humus layer samples and associated mineral soils representing each of the humus types were analyzed. A definite volume of sample (10 cc. of air-dry soil) was used, as suggested by Lunt (13). The leaching was accomplished by the use of Gooch crucibles and an automatic filtering device consisting of an inverted 500-cc. volumetric flask which was held just above the soil surface. In order to determine the amount of exchangeable hydrogen in the leachate, 50-cc. aliquots were titrated with 0.1 $N$ NaOH with phenolpthalein as the indicator. Blank aliquots of barium acetate were also titrated with 0.1 $N$ NaOH, and the value was subtracted from the leachate value. Duplicate determinations for each layer were made. The amount of exchangeable bases was determined by subtracting the amount of exchangeable hydrogen from the total base-exchange capacity.

## DESCRIPTION, DISTRIBUTION, AND ECOLOGY OF FOREST HUMUS LAYERS OF OHIO

The recent forest humus layer classification proposed by Heiberg and Chandler (8), has been found adaptable, with a few exceptions, for the humus layers of Ohio. This nomenclature is used, therefore, in the following descriptions.

### The mull group

*Coarse mull.* The coarse mull type can easily be distinguished in the field by the predominance of relatively large granules composed of mineral soil and very fine humus particles. The presence of the organic matter is generally indicated only by a dark gray color.[4] The size and form of the aggregates vary considerably, sometimes within a single habitat, but generally in different types of habitats. Usually the aggregates are from $\frac{1}{8}$ to $\frac{1}{4}$ inch in diameter and are slightly rounded. A layer composed entirely of such granules is naturally loose and porous. The depth of the coarse mull layers is most commonly from 2 to $2\frac{1}{2}$ inches; the maximum noted was 7 inches. Evidences of earthworms were

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[4] Photographs of profiles of a coarse mull, firm mull, and a matted mor which were analyzed for this investigation are used by Heiberg and Chandler (8) to illustrate these types.

generally found in this layer.    Ants are also prevalent in some areas and often have an effect upon the soil aggregation.    Roots of herbs, shrubs, and trees, from $\frac{1}{16}$ to $\frac{1}{4}$ inch in diameter, are usually numerous and evenly scattered throughout the mull layer.

In the description of this type, as given by Heiberg and Chandler (8), it is inferred, although not definitely stated, that the coarse mull layer merges gradually with the mineral soil beneath, generally the $A_2$ horizon.    In Ohio this sequence of horizons occurred in approximately half of the coarse mull profiles examined, whereas in the other half a compact nongranular humus layer occurred beneath the granular layer.    This second layer, which is generally designated as the $A_{11}$ horizon, appears to be very similar to the surface granular layer in all respects other than structure.    It is usually somewhat porous because of earthworm holes and roots and forms granules when a slight pressure is applied.    The usual depth is from 2 to 3 inches; layers from $\frac{1}{4}$ to 6 inches in depth were noted.

In the autumn, generally a layer of fresh hardwood leaves approximately 1 inch thick and a thin irregular layer of partly decomposed leaves (F layer[5]) cover the humus layer granules.

Coarse mull occurs throughout the state on many different types of topography, with a number of different soil types, and under various vegetation types.    The conditions under which it does not occur are as follows: in grazed or very open ungrazed woodlots, on the ridge tops and upper south slopes of the Unglaciated Plateau, on well-drained sandy soils, and on poorly drained areas which are periodically flooded.    Coarse mull is best developed in moderately well drained sites under virgin stands of mixed hardwoods.    It is generally associated with silt loam or silty clay loam mineral soils; however, the deepest layer of this type which was noted occurs on fine sand.

The site factors which aid in the development of coarse mull are also apparently favorable for the good growth of many hardwoods.    The most prevalent species[6] noted on this humus type were: white oak, red oak, sugar maple, beech, American elm, tulip tree, and black walnut.    Coarse mull was probably

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[5] The F layer consists of partly decomposed forest litter still recognizable as to origin.

[6] The following species of trees are mentioned in this paper:

| | |
|---|---|
| White ash *Fraxinus americana* | Swamp white oak *Quercus bicolor* |
| Basswood *Tilia americana* | Red oak *Quercus rubra* |
| Beech *Fagus grandifolia* | Bur oak *Quercus macrocarpa* |
| Black cherry *Prunus serotina* | Pin oak *Quercus palustris* |
| Chestnut *Castanea dentata* | Chestnut oak *Quercus Prinus* |
| American elm *Ulmus americana* | Black oak *Quercus velutina* |
| Slippery elm *Ulmus fulva* | Sassafras *Sassafras variifolium* |
| Witch hazel *Hamamelis virginiana* | Tulip tree *Liriodendron Tulipifera* |
| Pignut hickory *Carya glabra* | Black walnut *Juglans nigra* |
| Shell-bark hickory *Carya ovata* | Hemlock *Tsuga canadensis* |
| Magnolia *Magnolia acuminata* | White pine *Pinus Strobus* |
| Sugar maple *Acer saccharum* | Scrub pine *Pinus virginiana* |
| White oak *Quercus alba* | Short leaf pine *Pinus echinata* |

The common and the scientific names of plants are according to Gray's New Manual of Botany (15).

the dominant humus layer type associated with the original beech-maple type, the best drained phases of the swamp forest, and the mixed mesophytic types on the valley slopes. The shrub and herbaceous cover is variable from stand to stand, and because seasonal studies could not be made in this investigation, indicator species cannot be suggested.

The following site and soil profile description was made in one of the few remaining virgin stands in the state. The coarse mull is well developed and is typical in relatively undisturbed stands throughout the state.

Location of sample area: Hocking County, 10 miles northwest of the city of Logan near the town of Webb Summit.

Topography: Hilly with moderate slopes. Soil examined on north-facing slope. Drainage good.

Forest type[7]: White oak.

Soil type: Muskingum silt loam.

Soil profile:

1. A scattered uneven layer of fresh leaves over a $\frac{1}{2}$-inch layer of matted leaves. ($A_{00}$ horizon)

2. A thin irregular layer of partly decomposed leaves. (F layer)

3. 0 to $5\frac{1}{2}$ inches, gray granular silt loam which is a mixture of organic matter and mineral soil. The aggregates are uneven in size, varying from $\frac{1}{16}$ to $\frac{1}{2}$ inch in diameter, and form a loose porous layer which can be easily removed by hand from the layer beneath. Earthworm holes and excreta are abundant, especially on the surface. Small roots are scattered evenly throughout. ($A_1$ horizon)

4. $5\frac{1}{2}$ to $7\frac{1}{2}$ inches, gray firm silt loam, a mixture of organic matter and mineral soil which may extend to the surface in some places. This layer is partly porous because of the penetration of earthworm holes and roots, but forms aggregates only when subjected to a slight pressure. ($A_{11}$ horizon)

5. $7\frac{1}{2}$ to 12+ inches, yellowish brown silt loam which is very compact but can be easily broken into small aggregates. Sandstone fragments occur in this layer, and roots are distributed throughout. The transition to the above layer is generally sharp. ($A_2$ horizon)

6. Sandstone and shale occur below 20 to 30 inches. (C horizon)

Forest cover: One of the last virgin white oak stands in the state. It is an all-aged stand with approximately 70 trees per acre above 4 inches in diameter and 20 trees per acre over 20 inches in diameter. Nearly all of the trees are straight and well formed. White oak is the dominant species in the upper crown cover. In addition red oak, black oak, and hickory (*Carya glabra* and *Carya ovata*) are also important in local sections of the stand. Species of the ground cover which were noted are: *Cornus florida, Phryma leptostachya, Asarum canadense, Cryptotaenia canadensis.*

*Medium mull.* The structure of medium mull differs from that of coarse mull mainly in the size of the granules, which in the medium mull are approximately $\frac{1}{16}$ inch in diameter. This humus layer type varies in color from dark gray to dark grayish brown and generally blends gradually into the ligher colored mineral soil beneath. The average depth of the layer is 2 inches.

The medium mull layers which were examined for this investigation can be divided into two distinct subtypes mainly on the basis of the depth and structural characteristics of the layers. The mull layer of one subtype has an approximate

[7] The term "forest type" refers to the present cover type. It is designated by the dominant tree species which make up 50 per cent or more of the crown cover.

average thickness of 1 inch.   Roots are often matted on the surface of the mull, and no compact humus layer occurs beneath the granular mull.   The mull layer of the second subtype has an average depth of 2½ inches.   A compact humus layer, like that described for the coarse mull, is usually present beneath the granular layer.   Roots occur throughout the mull.   In the autumn, the litter layer is generally about 1 inch thick.   Beneath this, is an F layer, which is slightly thicker than that of the coarse mull.   Mycelia are sometimes visible throughout the layer.

Medium mull occurs throughout the state and is often associated with areas of coarse mull under various environmental conditions.   The first mentioned subtype occurs on silt loams under virgin as well as formerly grazed stands on the Till Plains and on the steep slopes of the Unglaciated Plateau.   The second subtype is more limited in distribution; it was found mainly on the fine sands and fine sandy loams of the Lake Plains.

Vegetation types associated with the medium mull are generally similar to those which occur with coarse mull.   The composition and structure of the wet beech type of Clermont County and the dry red oak-white oak type of Scioto County under which medium mull was found are different, however, from those of the vegetation types usually associated with the coarse mull. The most prevalent tree species on the medium mull are white ash, red oak, bur oak, beech, sugar maple, hickory, and American elm.

An example of a typical medium mull is described in the following site analysis:

Location of sample area: Clermont County, ⅛ mile west of Blowville.
Topography: Slightly undulating to level.   Soil examined on a level area.   Drainage
      poor.
Forest type: Wet beech.
Soil type: Clermont silt loam.
Soil profile:
1. 1 inch, very loose uniform layer of fresh leaves.   ($A_{00}$ horizon)
2. ¾ inch, flat and slightly compact layer of partly decomposed leaves.   Numerous mycelia
      are present.   (F layer)
3. 0 to 1 inch, dark gray silt loam aggregates of thoroughly mixed mineral soil and organic
      material which average $\frac{1}{16}$ inch in diameter and form a loose porous layer.   It is
      variable in thickness and structure with small changes in drainage.   A dense fine root
      layer occurs just under the upper surface; it can be easily removed, but not as a mat.
      Larger roots, about ⅛ inch in diameter, are scattered throughout.   ($A_1$ horizon)
4. 1 to 5 inches, light gray silt loam which breaks easily into soft powdery crumbs.   A few
      scattered roots occur throughout.   ($A_2$ horizon)
5. 5 to 10+ inches, mottled gray and yellowish brown silt loam.   A few scattered roots occur
      throughout.
6. Calcareous glacial drift occurs below 100 to 120 inches.   (C horizon)
Forest cover: An example of the wet beech type.   Beech is the main dominant; associate
species are red maple, white oak, tulip tree, and red gum.   It is an all-aged ungrazed stand
which has received numerous light selective cuttings.   The dominant trees are usually
15 to 20 inches in diameter and 50 to 60 feet high.   The stand is moderately well stocked.
The understory consists mostly of saplings and seedlings, very few shrubs, and the herbs
*Laportea canadensis, Eupatorium perfoliatum,* and *Impatiens biflora.*

*Firm mull.*   The fact that firm mull is a dense, compact, and generally struc-
tureless humus layer seems to be in conflict with the original characterization

of mull by Romell and Heiberg (16), who stated that a distinctive feature was its crumby or granular structure. In fact, a firm mull was not mentioned in the first American classification. Later it was found to be an important type and is considered as mull because it is a mixture of organic material and mineral soil which blends gradually with the mineral soil beneath.

Firm mull occurs on low poorly drained areas and to a large extent in open grazed upland woodlands. Many of the humus layers of the poorly drained areas are as much as 12 inches thick. The upper part of this mull layer can be broken more easily into aggregates, is slightly darker, and contains more roots than the lower part. In the better drained grazed woodlands, the entire humus layer is relatively thin, generally 3 to 5 inches in thickness, but has a structure similar to the thicker layer. The litter layer is usually scattered and mixed with the grass and sedge cover.

The firm mull has the same general distribution as the coarse and medium mull because a large proportion of it has developed from these two types as a result of the grazing and opening of the original forests. Although it was found in undisturbed forests only in the Wisconsin drift areas and on the Lake Plains, it probably occurs also on undisturbed sites in other parts of the state as a part of intrazonal soils such as the Wiesenboden.

Swamp forest communities are the characteristic vegetation of the undisturbed firm mull sites. The dominant forest trees noted on these habitats were American elm, white ash, red maple, swamp white oak, and bur oak. The dominant ground cover was generally species of grasses and sedges. The forest types which occur on the grazed firm mull sites are similar to those listed for the coarse mull and medium mull sites. These woodlands are generally open, especially if the grazing has been intensive. Environmental conditions resulting from the opening of the stands and the trampling of the livestock may have a detrimental effect on tree growth (7).

The description of a firm mull in a poorly drained ungrazed woodland is given in the following detailed site study:

Location of sample area: Franklin County, in a woodland of the Ohio State Experimental Farm, Columbus.

Topography: Undulating to level. Soil examined on a low level area. Drainage poor.

Forest type: American elm-white ash-red maple.

Soil type: Brookston silty clay loam.

Soil profile:

1. A thin uneven layer of fresh leaves over a few scattered, almost completely decomposed old leaves. ($A_{00}$ horizon)
2. 0 to 3 inches, dark gray compact mixture of silty clay loam and humus material. It is nonporous, but breaks easily into coarse aggregates. Earthworms are sometimes present, and their excreta occur as a thin granular layer on the surface of compact mull. Small roots are distributed evenly throughout.
3. 3 to 6½ inches, dark gray silty clay loam similar to the above layer but more compact and less easily broken into aggregates.
4. 6½ to 10½ inches, mottled dark gray and yellowish brown compact silty clay loam, a mixture of mineral soil and organic matter which has been influenced by a high water table. A few small roots occur throughout. (Firm mull includes horizons from 0 to 10½ inches.)

5. 10½ to 17+ inches, a mottled light gray and yellowish brown clay.

6. Calcareous glacial drift occurs below 30 to 40 inches.

Forest cover: The large timber was removed from this tract about 40 to 50 years ago. As a result, many of the dominant trees are approximately even aged and are mostly in the small timber or pole size classes. In a poorly drained local area near the soil pit, the stand is partly open and has an undercover of grasses and sedges.

*Fine sandy mull.* This mull type has not been defined in any classification for the United States. It is proposed as a new type because it has a number of characteristics which are different from those of types previously described. Because this humus layer is composed of a mixture of sand and humus material in the form of single grains and fine granules, the term "fine sandy mull" is proposed as a name for it. The humus substance is very fine in texture and is thoroughly mixed with the mineral soil particles. Because of its structure, the whole layer is porous and loose and can be easily removed from the mineral soil

TABLE 1

*Distribution of humus layer samples according to organic matter content classes*

| PERCENTAGE OF ORGANIC MATTER BY WEIGHT | 0–10 | 11–20 | 21–30 | 31–40 | 41–50 | 51–60 | 61–70 |
|---|---|---|---|---|---|---|---|
| HUMUS TYPE | | | | | | | |
| Coarse mull ($A_1$ horizon) | 11 | 3 | | | | | |
| Medium mull ($A_1$ horizon) | 1 | 5 | | | | | |
| Firm mull ($A_1$ horizon) | 2 | | | | | | |
| Fine sandy mull ($A_1$ horizon) | 3 | | | | | | |
| Twin mull (H layer) | | 2 | 1 | | 1 | | |
| Twin mull ($A_1$ horizon) | 1 | 3 | | | | | |
| Matted mor (H layer) | | 1 | 1 | 1 | | | |
| Granular mor (H layer) | | | | 1 | | | 1 |

surface by hand. It is dark gray to very dark gray and appears to have a high organic matter content, although this is actually relatively low (table 1). Small roots are scattered throughout. Figure 2 illustrates this humus type.

At first the fine sandy mull was considered as a fine mull because of its fine granular structure and dark color. Further investigation, however, revealed that its characteristics were entirely unlike those of a fine mull. The average organic matter content of the fine sandy mull is 9.4 per cent, whereas that of the fine mull, according to Heiberg and Chandler (8), is usually over 50 per cent. Layers of fine sandy mull 3 to 10 inches thick were noted; fine mull is generally more shallow in depth. The F layer of the fine sandy mull is poorly developed or missing, whereas that of the fine mull is usually ½ to 1 inch thick.

Very little is known about the exact distribution of the fine sandy mull, because only two areas containing it were investigated. It is necessarily limited to the sandy soils of the state, which are mainly in the Lake Plains and to some extent in the Unglaciated and Glaciated Plateaus. It was found on areas where the drainage is not excessive, in the one case on a flat sandy area which has a substratum of clay, and in the other on a slope which receives some seepage

water. This humus type was also noted on similar habitats on the Ontario Lake Plains of New York State.

Sites in which the fine sandy mull occurred appeared to be especially favorable for excellent tree growth. One of these areas is herewith described:

Location of sample area: Sandusky County, 5 miles west of Bellevue.
Topography: Gently rolling. Soil examined on a level area near the top of a hill. Drainage fair.
Forest type: Mixed hardwoods.
Soil type: Wauseon fine sandy loam.
Soil profile:
1. 1 inch, loose fresh leaves, evenly distributed. ($A_{00}$ horizon)
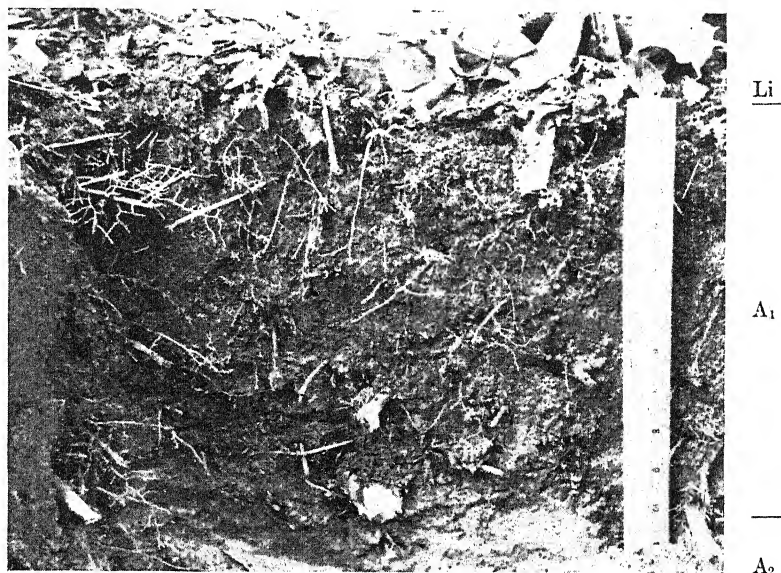


FIG. 2. PROFILE VIEW OF A FINE SANDY MULL

This dark fine-grained humus layer is very porous. Note that the roots are evenly distributed throughout the whole layer.

2. $\frac{1}{4}$ inch, slightly compacted layer of leaf fragments which are almost entirely decomposed. Mycelia are present and decomposition is apparently rapid. (F layer)
3. 0 to 10 inches, very dark gray fine sandy loam. It is a loose single-grained and fine granular mixture of sand mineral soil and black humus material. Small roots, from $\frac{1}{16}$ to $\frac{1}{4}$ inch in diameter, are distrbuted evenly throughout; a few larger roots, from $\frac{1}{2}$ to 1 inch in diameter, are all below 8 inches in depth.
4. 10 to 14+ inches, grayish brown loose fine sand. A few scattered roots occur throughout.
5. Clay occurs below 24 to 30 inches.

Forest cover: An ungrazed farm woodland which has been cut over but is still fairly well stocked. There are approximately 50 trees of the pole and small timber sizes per acre. The trees are well formed, and the growth is rapid as shown by ring counts. The stand is composed of a mixture of the following species: sugar maple, slippery elm, white ash, red oak, basswood, black cherry, and American elm. There are very few shrubs, and the tree reproduction is very sparse, but the following herbs cover from 30 to 50 per cent of

the ground surface: *Asarum canadense*, *Pilea pumila*, *Smilacina racemosa*, *Solidago latifolia*, *Eupatorium urticaefolium*, *Cryptotaenia canadensis*, *Polygonum virginianum*.

*Twin mull.*   The twin mull, as the name indicates, is composed of two humus layers, but not necessarily two mull layers; it may be composed of a mor type over a mull type.   In Ohio three different combinations were examined: a matted mor over a medium mull, a matted mor over a fine sandy mull, and a fine mull over a coarse mull.

The largest area of twin mull is probably on the Unglaciated Plateau in southern Ohio on south-facing slopes and ridge tops, habitats on which the matted mor has also developed.   On these sites the humus layer is composed of a matted mor over a medium mull or a fine sandy mull layer.   The component layers are not generally well developed.   There is usually a definite F layer $\frac{1}{2}$ to $\frac{3}{4}$ inch thick.   Beneath this is an H layer with an average thickness of $\frac{3}{4}$ inch, which occurs over a mull layer 1 inch thick.   The twin mull composed of a fine mull over a coarse mull occurs on poorly drained sites.   The fine mull, which has not been separately described, is characterized by its fine granular structure and high organic matter content.   A good example of this subtype occurs on poorly drained clay soil in northwestern Ohio; it has a thin F layer, a fine mull layer $\frac{1}{2}$ inch thick, and a 3-inch coarse mull layer.

The twin mull in Ohio may be considered as a transition type between the two humus type groups, an assumption that may be inferred from its composition. The twin mull occurs under environmental conditions which do not favor the complete development of either a mor or a mull.   In Ohio these conditions are found on very dry or very wet sites.   The matted mor–medium mull or matted mor–fine sandy mull subtypes are characteristic of the dry habitats.   These sites do not favor rapid tree growth or a high volume of timber, judging from the height and diameter of the dominant trees and the density of the stands, especially on the ridge tops.   White oak, red oak, and black oak are the most characteristic species under which the twin mull has developed; scrub pine, shortleaf pine, and hickories are also important in local areas.   Species of blueberry are distinctive of the ground cover.   This mull type was probably associated with the original forest associations of oak-hickory, oak-chestnut, and oak-pine.   The fine mull–coarse mull was found only in swamp forests.   The dominant tree species of these stands are: American elm, white ash, pin oak, swamp white oak, and red maple.

An example of a twin mull characteristic of the Unglaciated Plateau area of southern Ohio is given in the following description:

Location of sample area: Adams County, 3 miles northwest of West Union.
Topography: Moderate slopes.   Soil examined on a level area near the top of a hill.
Forest type: Oak-hickory.
Soil type: Bentonville silt loam.
Soil profile:
1. $1\frac{1}{2}$ inches, loose layer of fresh leaves, mostly oak.   ($A_{00}$ horizon)
2. $\frac{1}{2}$ inch, compact layer of partly decomposed oak leaves.   Mycelia are numerous.   (F layer)

3. ¼ inch, dark grayish brown layer which has a high organic matter content. It is composed of very fine humus particles, small partly decomposed pieces of organic matter, and mineral soil grains which occur together as single grains and small aggregates. The layer occurs as a mat which may be removed in small pieces. Few roots are scattered through it. The entire layer is compact but light in weight. (H layer)

4. 0 to ½ inch, grayish brown granules $\frac{1}{16}$ inch in diameter with some larger aggregates. These particles are composed of a mixture of humus material and silt loam mineral soil. The layer is loose and porous and is penetrated by a large number of small woody roots. (A₁ horizon)

5. ½ to 5 inches, grayish brown compact silt loam which breaks into powdery single grains or small granules. A few scattered roots occur throughout. (A₂ horizon)

6. 5 to 10+ inches, yellow-brown compact silt loam.

7. Bedrock is composed of limestone and shale.

Forest cover: This is essentially a pole stand with a few larger scattered trees, a condition which is a result of a former heavy cutting. However, the stand is well stocked. Seedlings are numerous, but the shrub and herbaceous cover is sparse. Three species of oak, red, white, and black, and two species of hickory (*Carya glabra* and *Carya ovata*) form the dominant tree cover. Shrub species noted were: *Amelanchier canadensis*, *Cornus florida*, *Circis canadensis*, *Sassaras variifolium*.

### The mor group

*Matted mor.* The matted mor type can be easily distinguished in the field because of its clear-cut characteristics. An F layer is usually present; on some habitats it is from ⅛ to ½ inch thick. The underlying H layer is dark brown or grayish black, light in weight, and is penetrated by a dense mass of intertwining roots which bind the whole layer together so that it can be removed as a mat from the surface mineral soil; the average thickness is from 1 to 1½ inches. Because of the dark color and light weight of this layer, it appears that it is almost entirely organic in composition. Laboratory tests, however, show that it contains only 22 to 35 per cent organic matter by weight. The line of demarcation between the H layer and the mineral soil is usually very sharp, although in some cases there is a small transition layer which results from the washing of some organic matter into the mineral soil.

The matted mor type was found only on two types of habitats: on the deep sands of the "Oak Openings" of the Lake Plains, and on the silt loams of the ridge tops and upper south slopes of the Unglaciated Plateau. Both sites are well drained and dry, especially during the latter part of the summer and early autumn. The mineral soils are decidedly acid and appear to be unsuitable for good plant growth.

Although the two areas differ in many respects, the vegetation of both is somewhat similar in floristic composition and general aspect. Forests of both sites are characterized by moderately poor stocking, relatively small height and diameter of the trees, and fairly dense ground cover of shrubs. White oak and black oak are common to both areas as well as species of blueberry, huckleberry, and wintergreen. In the "Oak Openings," white oak and black oak are generally the dominant tree species, frequently comprising 90 per cent of the crown cover. Witch hazel and sassafras are the characteristic shrubs. In the stands on the Unglaciated Plateau, chestnut oak is frequently the main dominant, and

in addition to white oak and black oak, shortleaf pine and scrub pine are often scattered in the stands. In the past, chestnut was an additional dominant.

In view of the fact that the laminated mor type in Ohio is very similar to the matted mor in structure and ecology as well as in physical and chemical characteristics, it is questionable whether it should be designated as a separate type. By definition it differs from the matted mor only by its thicker F layer. It occurs in the "Oak Openings" with an F layer $1\frac{1}{2}$ inches thick in habitats which are very similar to those in which the matted mor developed. Only a few observations and analyses of the laminated mor type were made during this investigation, but on the basis of these it is the opinion of the author that it should not be considered as a separate humus type, and the possibility of making it a subtype of the matted mor is suggested.

The following is a detailed description of a matted mor type:

Location of sample area: Lucas County, $\frac{3}{10}$ mile west of Whitehouse.
Topography: Undulating to gently rolling. Soil examined on the top of a small hill. Drainage good.
Forest type: White oak-black oak.
Soil type: Plainfield fine sand.
Soil profile:
1. A loose continuous layer of fresh leaves. ($A_{00}$ horizon)
2. $1\frac{1}{2}$ inches, compacted laminated layer of slightly decomposed oak leaves. Mycelia are numerous, and the decomposition is slow. (F layer)
3. $1\frac{1}{4}$ inches, a dark brown layer with a high organic matter content. It is composed of single grains and small aggregates of very fine humus particles and sand. The whole layer is penetrated by a mass of small roots. The soil particles cling to the roots so that the horizon forms a mat which can be removed in large pieces from the layer below. (H layer)
4. 0 to $\frac{1}{2}$ inch (often missing), grayish brown sand which is mixed with a small amount of organic matter. ($A_1$ horizon)
5. $\frac{1}{2}$ to 15+ inches, yellowish brown fine sand. ($A_2$ horizon)
6. Sand or a noncalcareous sand and gravel mixture from 60 to 120 inches in depth. (C horizon)

Forest cover: A heavily cut-over ungrazed woodland which is typical of the "Oak Openings." The stand is poorly stocked, and the crown cover is open. The trees are small, and the growth is slow as shown by ring counts. The oaks are 13 to 18 inches in diameter and 30 to 40 feet in height. Poles, saplings, and seedlings are sparse or missing over large sections. Shrubs, common among which is witch hazel, and herbs form a dense cover. Species of blueberry and huckleberry cover 80 per cent of the ground in some areas. Black oak and white oak are about equally distributed and make up approximately 90 per cent of the crown cover.

*Granular mor.* The area of granular mor in Ohio is apparently small; only two sites with this humus layer type were located. The litter layer is $\frac{1}{2}$ to $\frac{3}{4}$ inch thick, and the F layer $\frac{1}{2}$ inch thick. The H layer, 2 to 3 inches deep, is composed of fine black soil granules in a loose porous formation. Numerous small fibrous roots occur throughout the layer, but no root mat is formed. The mineral soil layers beneath consist of a gray sandy eluvial layer, a reddish brown illuvial layer, and stony parent material. This is a true podzol profile (fig. 3) which is similar to those found farther north in the coniferous belt. The layers investigated in Ohio developed under white pine and hemlock, on one site in Ashtabula

County and one site in Lake County. This type probably exists on other coarse-texture soils in northeastern Ohio, especially under softwoods. The following is a description of the white pine-granular mor site which occurs in Lake County:

Location of sample area: Lake County, 1 mile west and 4 miles south of Painesville.
Topography: Moderate slopes. Soil examined near the summit of Little Mountain on a slight north-facing slope. Drainage good.
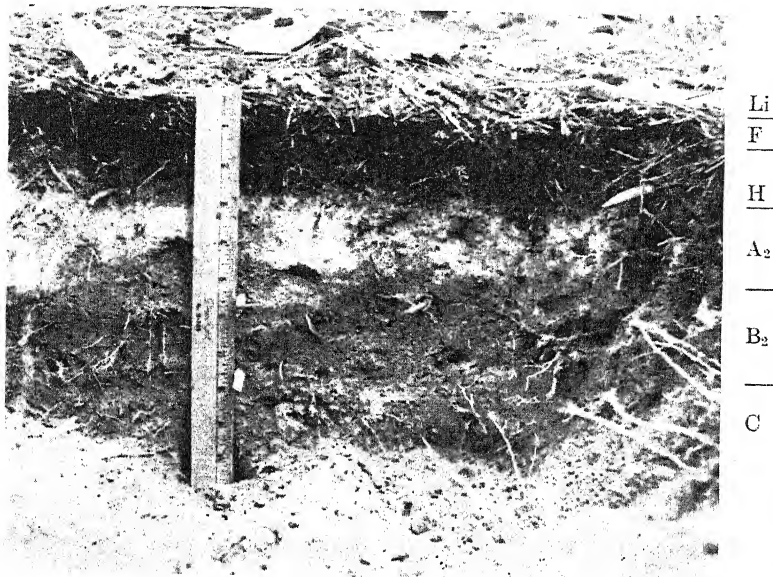Forest type: White pine.



FIG. 3. A GRANULAR MOR LAYER WHICH OCCURS IN A WHITE PINE STAND IN NORTHEASTERN OHIO

The humus layer is composed of partly decomposed needles (F layer), which cannot be distinguished in the photograph, and an H layer 2½ inches thick. Roots occur throughout the H layer, are almost entirely absent in the eluvial layer, and are abundant in the B horizon.

Soil type: Lordstown stony loam.
Soil profile.

1. ½ inch, undecomposed pine needles with a few red maple and witch hazel leaves. This layer is fairly loose but somewhat laminated; it can be removed in small mat-like pieces ($A_{00}$ horizon)

2. ½ inch, very dark brown compact layer of partly decomposed needles. This blends gradually into the layer below, and therefore the lower boundary is indistinct. (F layer)

3. 2 inches, black granules composed of small pieces of partly decomposed organic material, fine particles of humus, and a small amount of sand. The granules are small, generally less than $\frac{1}{16}$ inch in diameter, and loose; the whole layer can be removed easily by hand from the layer below. Small fibrous roots are distributed evenly throughout. Mycelia are sparse. (H layer)

4. 0 to 2 inches, gray compact sandy loam which breaks easily into single grains. A few small roots are scattered throughout the horizon. ($A_2$ horizon)

5. 2 to 3 inches, reddish brown sandy loam. Roots occur throughout the layer. (B$_2$ horizon)

6. 3 to 15+ inches, yellowish brown stoney loam. (C horizon)

Forest cover: A virgin white pine stand. It is an all-aged moderately well stocked woodland which is open only where dead trees have been removed (mainly chestnut). The largest and oldest trees are white pine, many of which are 26 to 31 inches in diameter and 70 to 80 feet in height. All of the pines are in the medium and large timber classes whereas other species in the stand, mainly red maple, hemlock, beech, sugar maple, and magnolia, are in the pole size class. The shrubs *Hamamelis virginiana, Viburnum acerifolium, Sambucus racemosa, Smilax rotundifolia, and Cornus alternifolia;* the herbs *Maianthemum canadense* and *Aralia nudicaulis;* and the fern *Aspidium spinulosum* are sparse and well scattered.

## Humus layers of coniferous plantations

Investigations were made in two of the oldest coniferous plantations in the state for the purpose of comparing the humus layer development with that of natural stands. The humus layer which is herewith described has developed under a 30-year-old white pine plantation. This layer appeared to be a firm mull; however, by further investigation it was found that it differs from the previously described firm mull in that it has a higher organic matter content, includes partly decomposed litter, is lighter in weight per unit volume, and has a definite F layer. It apparently is the "poorly humified type" described by Junker and which Romell and Heiberg (16) say is the common plantation type in this country. A humus layer which has developed in a 32-year-old red pine stand in southeastern Ohio closely resembles a twin mull.

The following is a description of the humus layer of the white pine plantation:

Location of sample area: Wayne County, Ohio Agricultural Experiment Station Arboretum
Topography: Rolling. Soil examined near the top of a small hill. Drainage good.
Plantation type: White pine.
Soil type: Wooster silt loam.
Soil profile:

1. 1 inch, loose undecomposed pine needles. (A$_{00}$ horizon)

2. $\frac{3}{4}$ inch, spongy layer of partly decomposed needles which is compact and can be removed in small mat-like pieces. (F layer)

3. 0 to $\frac{1}{2}$ inch, dark gray firm horizon which is composed of a mixture of mineral soil, humus material, and some partly decomposed needle fragments. It is compact and distinctly nongranular *in situ* but breaks into fine single grains. (A$_1$ horizon)

4. $\frac{1}{2}$ to 8+ inches, light brown compact silt loam. A few scattered roots occur throughout. (A$_2$ horizon)

5. Glacial drift of sandstone and shale occurs below 30 to 36 inches.

Plantation cover: A pure white pine stand which was planted in 1911. The trees vary in diameter from 4 to 8 inches and from 40 to 50 feet in height. During some years the maximum height of growth was 24 to 35 inches. Shrubs and herbs are sparse in the stand.

### PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE FOREST HUMUS LAYERS

## Organic matter content

One of the most apparent differences between the mull group and the mor group is the higher organic matter content of the latter. Laboratory analyses also indicated this difference, as shown in table 1. The medium mull, which in

most cases is relatively light in color, has a higher content than was anticipated, whereas the dark-colored fine sandy mull has a lower content. The organic matter content of the $A_2$ horizons is lower in all samples than that of the associated humus layers; it varies from 1 to 4 per cent.

The average organic matter content of the humus layer types of Ohio is lower than that of similar layers in northeastern United States (12). There is only a small difference between the coarse mulls and the twin mulls, but the matted mor and laminated mor types of the Northeast have a much higher content than similar layers in Ohio.

### Moisture equivalent

There is no distinct group difference between the moisture equivalent values of the mull and mor layers (table 2); however, the range of values for the mull layers, 15 to 36 per cent, is lower than the range for the mor layers, 23 to 42 per cent. Each humus layer has a higher moisture equivalent value than the mineral soil beneath it, which indicates a correlation with the organic matter content. The data of Lunt (12) show that with soils of the same texture there is a correlation between the organic matter content and the moisture equivalent; in general, the higher the organic matter content, the higher the moisture equivalent. The values obtained by Lunt for mulls on fine sandy loam are considerably lower than the Ohio values.

### Acidity

In general, the acidity of the mull group is lower than that of the mor group, but there are considerable variations in each group, and consequently no definite line can be drawn between the groups, as shown in table 3. The pH values for the medium mull fall within the same range as those of the mor group and the values of both layers of the twin mull vary from the neutral range to high acidity. The humus layers generally have a higher pH value than that of the mineral soil beneath. The values of the coarse mull layers range from 7.0 to 6.1, whereas the range of the associated mineral soils is from 4.4 to 6.6. The H layers of the mor group are sometimes exceptions to this relationship. The pH values of the humus layers of Ohio are generally higher than those obtained by Romell and Heiberg (16) for similar layers of the northeastern soils.

### Exchange complex

The character of the exchange complex of each humus type is shown in figure 4. The three most common mull types have approximately the same total exchange capacity The higher capacity of the fine sandy mull is similar to that of the matted mor. The very high capacity of the granular mor is over twice that of the mulls. The difference between the mull and mor groups can be correlated with the difference in organic matter content. This relationship has been shown by McGeorge (14), who found that in highly organic soils the exchange capacity is a linear function of the percentage of total carbon in the soil. The total

TABLE 2

*Moisture equivalent of humus layers and associated mineral soils*

In per cent

| HUMUS TYPE | SOIL TYPE | MOISTURE EQUIVALENT | |
|---|---|---|---|
| | | Humus layer | Surface mineral soil |
| Coarse mull | Miami silty clay loam<br>Muskingum silt loam | (A₁ Horizon)<br>35.21<br>33.53 | (A₂ Horizon)<br>24.72<br>29.27 |
| Medium mull | Canfield silt loam<br>Clermont silt loam<br>Crosby silty clay loam | (A₁ Horizon)<br>29.16<br>32.78<br>31.01 | (A₂ Horizon)<br>21.38<br>24.48<br>21.58 |
| Firm mull | Brookston silty clay loam | (A₁ Horizon)<br>35.73 | (A₂ Horizon)<br>30.28 |
| Fine sandy mull | Wauseon fine sandy loam<br>Unnamed sand with Muskingum silt loam | (A₁ Horizon)<br>22.59<br>30.37 | (A₂ Horizon)<br>7.41<br>10.48 |
| Twin mull | Unnamed sand with Muskingum silt loam | (H layer) (A₁ layer)<br>42.45    15.27 | (A₂ Horizon)<br>7.82 |
| Matted mor | Muskingum silt loam<br>Plainfield fine sand | (H layer)<br>28.57<br>23.02 | (A₂ Horizon)<br>18.50<br>3.38 |
| Granular mor | Lordstown loam | (H layer)<br>42.40 | (A₂ Horizon)<br>7.42 |

TABLE 3

*Distribution of humus layer samples according to pH classes*

| pH CLASSES | 7.5–7.1 | 7.0–6.6 | 6.5–6.1 | 6.0–5.6 | 6.5–5.1 | 5.0–4.6 | 4.5–4.1 | 4.0–3.6 |
|---|---|---|---|---|---|---|---|---|
| **HUMUS TYPE** | | | | | | | | |
| Coarse mull (A₁ horizon) | 1 | 6 | 4 | 2 | | 1 | | |
| Medium mull (A₁ horizon) | | 1 | | | 1 | | 3 | 1 |
| Firm mull (A₁ horizon) | 1 | 1 | | | | | | |
| Fine sandy mull (A₁ horizon) | 1 | 1 | | | | | | |
| Twin mull (H layer) | | 1 | 1 | | 1 | | 1 | |
| Twin mull (A₁ horizon) | | 1 | | 2 | 1 | | | |
| Matted mor (H layer) | | | | | 2 | 1 | | |
| Granular mor (H layer) | | | | | | | | 2 |

exchange capacity of the mineral soils is also of importance. The values for the mineral soils associated with the mull types, which are mostly silt loams, are slightly higher than those for the soils associated with the mor types, which are

mainly sands and sandy loams. This is probably due to the higher percentage of colloidal material in the silt loams than in the sands.

There is a very evident difference between the mull types and the mor types (with the exception of the medium mulls) in the degree of saturation of exchangeable hydrogen and exchangeable calcium. The mulls have a relatively high percentage of calcium, whereas the mors have a high percentage of hydrogen. However, the absolute amounts of exchangeable calcium of both groups are not greatly different. The surface mineral soils generally have a higher percentage
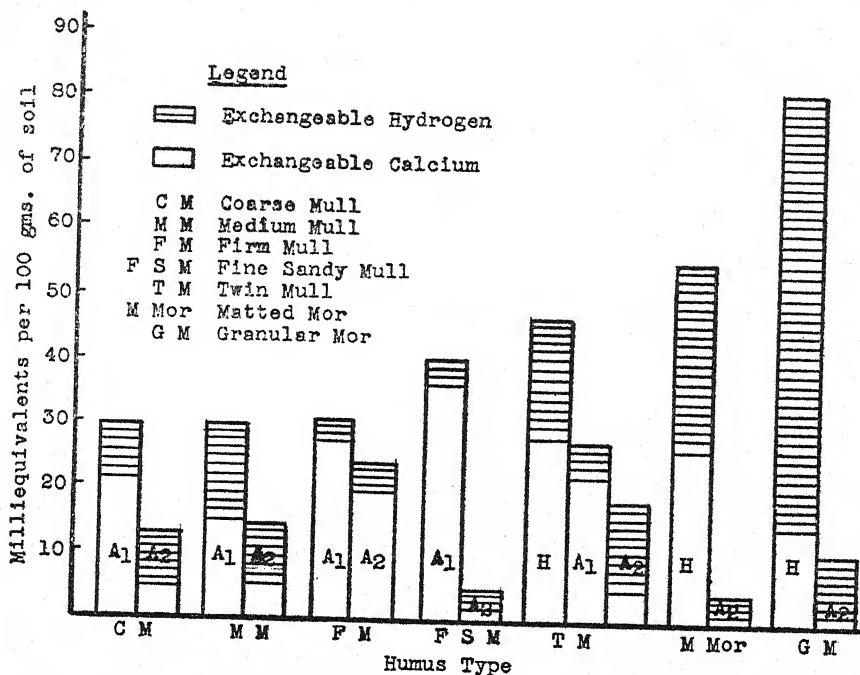


FIG. 4. AVERAGE TOTAL EXCHANGE CAPACITY, EXCHANGEABLE HYDROGEN, AND EXCHANGEABLE CALCIUM FOR EACH HUMUS LAYER TYPE AND ASSOCIATED MINERAL SOIL

of exchangeable hydrogen than the humus layers which have developed on them. This relationship is more pronounced in the mor types than in the mull types.

The mull and mor humus layer types of Ohio have, in general, a lower total exchange capacity, a lower amount of exchangeable hydrogen, and a greater degree of base saturation than similar types in the Adirondacks cited by Chandler (4). In all cases the organic matter content of the Adirondack types is higher than that of the Ohio types.

## SUMMARY

The recently proposed nomenclature of the forest humus layers for the northeastern United States by Heiberg and Chandler (8) can be used to classify the forest humus layers of Ohio. One additional type and four subtypes are de-

scribed, and a combination of two other types is recommended. Characteristic features of each of the types of Ohio may be summarized as follows:

The coarse mull occurs typically on fairly well to well-drained silt loams and silty clay loams in well-stocked hardwood stands. It is associated with many different soil and forest types throughout the state. A compact structureless humus layer beneath the granular surface humus layer is characteristic of many of the coarse mulls of Ohio.

The medium mull type was found in habitats similar to those described for the coarse mull. It occurs as a relatively thick layer on fine sandy loams of the Lake Plains and as a shallow layer on the dry ridge tops of the Unglaciated Plateau and on poorly drained silt loams of the Illinoian drift area.

A large area of the firm mull has developed as the result of the partial deforestation and grazing of woodlands which originally had other humus layer types. In undisturbed stands, it occurs mainly on poorly drained sites.

The fine sandy mull is a type which has not been described previously in the United States. It is a dark gray mixture of sand and fine granular humus material. Superficially, it resembles a fine mull; it differs from this type in that it has a much lower organic matter content, a poorly developed F layer, and occurs to a greater depth. It was found on a fine sandy loam in northern Ohio and on a sand in southern Ohio, in both cases under a mesophytic forest type.

The twin mull may be divided into two subtypes which have different characteristics. One subtype occurs mainly on the dry ridges and southfacing slopes of the Unglaciated Plateau; it is composed of a matted mor over a medium mull or fine sandy mull. White oak, red oak, black oak, and species of blueberry are characteristic of these sites. The second subtype, which is composed of a fine mull over a coarse mull, occurs on poorly drained clays of the Lake Plains under swamp forest tree species.

The matted mor and laminated mor types are so nearly alike that it is suggested that they be combined into one type, the matted mor. This type occurs on two entirely different sites: on the deep well-drained sands of the "Oak Openings" of northern Ohio, and on the dry ridges and upper south-facing slopes of the Unglaciated Plateau. White oak, black oak, huckleberry, wintergreen, and species of blueberry are characteristic on both habitats.

Granular mor was found only under softwoods on sandy or stony loams in northeastern Ohio.

The organic matter content (by weight) of the mor types, which varies from 18 to 61 per cent, is generally greater than that of the mull types, which varies from 5 to 20 per cent. The acidity of the humus layers of the mull group is generally less than that of the humus layers of the mor group; the pH values of the mull range from 4.7 to 7.3, and those of the mor from 3.7 to 6.3. The total exchange capacity of the mulls is relatively low in comparison with that of the mor types, but the degree of base saturation is generally higher in the mull group than in the mor group. Moisture-equivalent values of the mull layers range from 13 to 36 per cent, and those of the mor layers from 23 to 42 per cent.

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# NITRATES TESTS FOR SOILS AND PLANT TISSUES[1]

## ROGER H. BRAY[2]

*Illinois Agricultural Experiment Station*

The available forms of nitrogen in soils, such as nitrate and ammonia, vary considerably in amount not only from season to season but from week to week and from day to day. The actual amount found in the soil at any one time is likely to have little significance as an indication of the amount that will become available to crops during the growing period. Nitrate measurements during the spring, before crops start to feed heavily, probably have the most significance. But once crops start to develop, even though the amounts of nitrates being liberated by soil organisms might be ample for good yields, yet the soil itself might be practically devoid of nitrates during the rest of the season because uptake can occur about as rapidly as the nitrates are formed. This situation is not true for the majority of the plant nutrients in most soils. The available forms of phosphorus, potassium, calcium, and magnesium, for example, are readily built up to a high level, which can be maintained from year to year. They are not subject to appreciable leaching, and the amounts present are a good index of the fertility of the soil with respect to these nutrients and its need for them during the coming season and often for a period of years.[3]

To study nitrogen fertility, therefore, it is not sufficient to run one soil test or tissue test for the presence of nitrates. Instead, one must study the nitrate supply in the soil and in the plant growing on the soil during the whole season.

It is the purpose of this paper to describe two tests for nitrate nitrogen in soils and plants. These tests have certain advantages over the usual diphenyl-amine method, which employs concentrated sulfuric acid and which is used extensively for tissue tests. The first method is a modification of one which has already been described in a pamphlet released by this station.[4] The second uses a dry powder containing all the reagents. The tests have been used during the past two seasons in a study of seasonal changes in the nitrate content of soil and plant tissue and have been found satisfactory for these purposes.

## DESCRIPTION OF THE TESTS

The tests are based upon the formation of a pink dye through the interaction of nitrous acid with alpha-naphthylamine and sulfanilic acid in an acid medium.[5]

Both methods employ manganous sulfate, which helps prevent interference from chlorides and gives a more nearly quantitative reduction of nitrate to nitrite. These methods are specific for the combined amounts of nitrate and nitrite.

## Method 1

*Reagent 1.*          (a) 100 gm. $BaSO_4$

                      (b)   1 gm. finely powdered zinc

                      (c)  10 gm. $MnSO_4 \cdot H_2O$

The reagents should be free of nitrate and nitrite and be thoroughly ground together, making a nearly white powder.

*Reagent 2.* Ten per cent acetic acid made nitrate-free by the addition of a little powdered zinc.

*Reagent 3.* To 50 ml. of reagent 2 add approximately 0.25 gm. (size of a pea) of a mixture of equal parts by weight of alpha-naphthylamine and sulfanilic acid.

*Reagent 4.* A standard nitrate solution (100 p.p.m. of N).

*Procedure 1—For soil extracts or solutions.* Take 5 gm. of soil and 10 ml. of reagent 2 (or any salt or acid extracting solution, in any proportion, which will not interfere with the test). Shake together 1 minute and filter. To 1 ml. of the soil extract add 7 ml. of reagent 2 and, with a measuring spoon, $\frac{1}{2}$ ml. of reagent 1. Shake immediately for exactly 20 seconds. Add immediately 1 ml. of reagent 3 and allow to settle. Read the color by comparing with a series of nitrate standards developed in the same way. The colors fade slowly on standing. A set of permanent standards (calibrated with nitrate standards) can be made with acid fuchsin in 1 per cent acid saturated with camphor.

*Procedure 2—For use without filtering.* To 1 gm. of soil (or finely cut plant tissue), add $\frac{1}{2}$ ml. of reagent 1, then add 7 ml. of reagent 2 and immediately shake for exactly 20 seconds. Allow the mixture of soil and powder to settle, and add 1 ml. of reagent 3.

In this case the colors are read by comparing with colors produced by testing similar soils containing known amounts of nitrate or standards based on such colors. This is necessary because the color obtained is less than that produced in the absence of soil. This method is more rapid but less accurate than procedure 1.

## Method 2 (Powder method)

*Reagent 5 (nitrate test powder).*

| | |
|---|---|
| (a) 100 gm. $BaSO_4$ | (d) 75 gm. citric acid |
| (b)  10 gm. $MnSO_4 \cdot H_2O$ | (e)  4 gm. sulfanilic acid |
| (c)   2 gm. finely powdered zinc | (f)  2 gm. alpha-naphthylamine |

Grind any coarse materials to a fine powder. Mix b, c, e, and f *separately* with portions of the $BaSO_4$. Then thoroughly mix the whole, including a and d. Use extreme care to have room, table tops, and equipment free of nitrate and nitrite. Store the powder in a thoroughly blackened bottle, as light affects the alpha-naphthylamine. It will keep several years in a bottle painted on the outside with black paint.

*Procedure 3*—To 1 ml. of soil extract, obtained as described under procedure 1, add 6 ml. of distilled or nitrate-free water and $\frac{1}{2}$ ml. of reagent 5. Shake for 25 to 30 seconds, and allow to settle. Read colors as described above.

*Procedure 4*—A rough test for soil nitrate can be made by measuring 1 ml. of reagent 5 into 1 gm. of soil in 7 ml. of distilled water. Shake this for 25 to 30 seconds, and allow it to settle. The test run in this way will not be very sensitive and is recommended only for preliminary exploratory work.

*Procedure 5*—Shake 1 measure of finely chopped plant material, 1 measure of reagent 5, and 14 measures of distilled water for 25 to 30 seconds and allow to settle. Read colors as described above.

*Procedure 6*—Split open or break off succulent plant tissue, apply a thin layer of reagent 5 to the freshly exposed surface, and squeeze material until the plant juices have wet the powder. Nitrates in the tissue are indicated by the powder's turning pink.

## DISCUSSION

Method 1 is sensitive to 1 p.p.m. of nitrate in solution yet covers a fairly wide reading range up to 35 to 50 p.p.m. When filtered and read in a photometer, replicates are reproducible to within 2 or 3 p.p.m. N in the range of 5 to 30 p.p.m. In this respect it is superior to the diphenylamine test usually used as a spot plate test which, although sensitive to traces of nitrate, is not specific and is difficult to read with much more than a plus or minus reading.

Method 1 is sufficiently rapid to be classified with the quick tests and, by appropriate dilutions of the extract, will cover the range of nitrates found in soils. It is fairly accurate, quantitatively, and could be made more so by centrifuging and reading the color in a photometer in comparison with similarly developed nitrate standards.

When method 1 is used as a direct test in the presence of the soil (procedures 2 and 4), adsorption by the soil decreases the amount of pink color obtained as compared to the tests on the extracted liquid. These uses of the methods should be confined to exploratory work or special calibrations worked out for each situation where more rapid procedures are wanted.

In tissue testing, method 1 permits a direct reading of the amounts of nitrate accumulated (when tissue weight is known). Again this is in contrast to the diphenylamine tissue test which gives a plus or minus reading and little indication of the actual amounts of nitrate accumulated in the plant tissue. The reagents are also easily handled in the field without the danger of burning skin or clothing, a disadvantage of the diphenylamine method.

Method 2 requires fewer reagents than method 1. When it is employed as a plant tissue test, enough reagent for many tests is readily carried in a small tube and used in the field by applying the dry powder to the cut parts of moist tissue, which furnishes the moisture for the reaction. Used in this way, it becomes more of a plus or minus indicator than a quantitative test. This is due to the fact that when small amounts of nitrate are present they continue to diffuse to the reacting surface and give, with time, an increasingly intense pink color. For exploratory work, however, the procedure is very satisfactory.

# PLANT NUTRIENT LOSSES IN SILT AND WATER IN THE TENNESSEE RIVER SYSTEM[1]

ELMER O. FIPPIN[2]

*Tennessee Valley Authority*

## BASIS OF INVESTIGATION

Some of the questions which naturally arise in a watershed protection program are: How much plant nutrient material is removed from the watershed in the silt and water in the river system? How does the loss in solution compare with the loss in silt? How do these losses compare with the losses through erosion that have been measured on particular plots of land of different soils, slope, and plant cover in other sections of the country, or with observed losses on particular small areas in the watershed? How does the nutrient content of the silt and water vary in relation to rock structure and soil character of the different sub-watersheds? This survey was undertaken to provide data on these questions as they relate to the Tennessee Valley watershed, as one more link in the chain of evidence of the destructive effects of accelerated erosion on the productive capacity of the soil, and the need for its control.

The Tennessee Valley is a region of 26 million acres, with an annual rainfall ranging from 40 to 80 inches, very diverse topography, rock structure, and soil character, where erosion is widespread and very active on many areas. It is therefore well adapted for a survey of plant nutrient losses.

The Authority was in a favorable position to make the investigation. For a number of years its Hydraulic Data Division had been measuring the stream flow at many points and collecting samples for the determination of silt content and had facilities for chemical analyses. Accordingly, arrangements were made between that division and the chief conservation engineer and the department of agricultural relations to carry out the study, under an advisory committee, on the sampling, range, and methods of chemical analysis, and the analysis and presentation of the data.

It is hoped that such surveys may be repeated at intervals of years, as the management and plant cover on the land are improved, in order to measure the efficiency of these methods in the conservation of soil and rainfall.

LOCATIONS, PERIODS OF SAMPLING, AND CHARACTERISTICS OF DRAINAGE AREAS

The locations from which samples of silt and water were collected for analysis, the period of sampling, the drainage areas above each sampling point, and the dominant features of the rock and soil formations of each watershed are shown in table 1. The distribution of these stations is shown in figure 1.

TABLE 1

*Location, dates of sampling, and drainage area above each location*

| LOCATION | | PERIOD OF SAMPLING | | DRAINAGE AREA | DOMINANT SOIL AND ROCK FORMATIONS OF WATERSHED |
|---|---|---|---|---|---|
| | | From | To | | |
| | | | | *square miles* | |
| *Tributary streams* | | | | | |
| Powell River at Arthur | Silt | 1/30/39 | 6/ 5/40 | 685 | Cherty dolomite, limestone, acid shale, and shale sandstone |
| | Water | 9/19/39 | 6/ 5/40 | | |
| Clinch River near Tazewell | Silt | 1/16/39 | 4/23/40 | 1,474 | Same as Powell, more limestone |
| | Water | 8/ 7/39 | 4/23/40 | | |
| Hiwassee River at Murphy | Silt | 1/30/39 | 9/20/39 | 421 | Ancient igneous and metamorphosed shale and sandstone, low calcium |
| | Water | 7/29/39 | 2/18/40 | | |
| Duck River near Hurricane Mills | Silt | 1/13/39 | 5/24/40 | 2,571 | Limestone and shale with considerable phosphatic limestone |
| | Water | 7/26/39 | 5/24/40 | | |
| *Main streams* | | | | | |
| Tennessee River at Knoxville | Silt | 2/ 4/39 | 5/ 2/40 | 8,913 | |
| | Water | 9/14/39 | 5/ 2/40 | | |
| Tennessee River at Chattanooga | Silt | 2/ 5/39 | 5/29/40 | 21,400 | Mixture Powell, Clinch, and Hiwassee formations |
| | Water | 1/13/39 | 5/29/40 | | |
| Tennessee River at Savannah | Silt | 1/31/39 | 4/ 2/40 | 33,140 | |
| Tennessee River at Johnsonville | Silt | 1/13/39 | 5/ 1/40 | 38,530 | Additions from phosphatic formations |
| | Water | 3/14/39 | 5/ 1/40 | | |
| Mississippi River near mouth | Silt | 6/14/38 | 5/31/39 | 1,244,000 | Wide variety |

The subwatersheds for sampling were selected to embrace different petrographic and soil type areas to determine the effect of these on the composition of the silt[3] and the drainage water.

The silt analyses covered approximately 1½ years, from January, 1939, to

[3] The term *silt* is used to embrace all material in suspension, irrespective of the size of particles.

June, 1940. The water analyses covered nearly 1 year, from July, 1939, to May, 1940. Both periods varied somewhat on the different watersheds.

Water samples collected at Savannah were found to contain very little silt, because of the desilting action of the reservoirs just above that point. Only a few samples were collected, therefore, and their analyses are omitted.

For comparison, it was thought desirable to obtain samples of silt from the lower Mississippi River, through the army engineers who make the measurements of flow and silt content of that river. A limited number of samples for a less complete cycle than for the Tennessee Valley streams were obtained and analyzed. These samples were taken in three main passes of the river through the lower
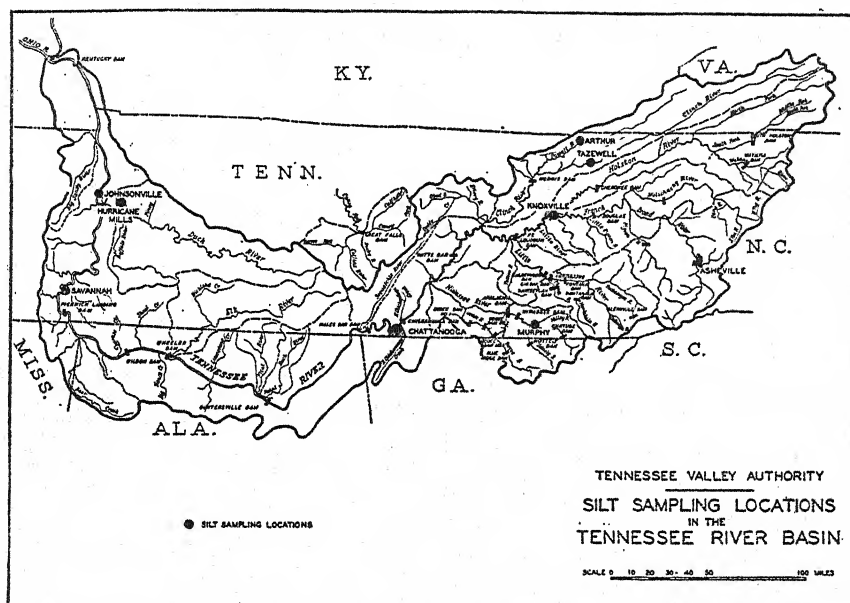


FIG. 1. LOCATION OF SAMPLING STATIONS ON TENNESSEE RIVER SYSTEM

delta a short distance above their discharge into the Gulf of Mexico. Because of differences in method of sampling, these measurements of the volume of silt are not strictly comparable with those taken in the Tennessee Valley.

## METHODS

### Collecting samples

In the Tennessee Valley, every time a field engineer visited a sampling location to collect silt samples in the regular investigations of the Hydraulic Data Division, one or more 5-gallon carboys were filled with water from the river with its normal load of silt. The silt was allowed to settle for 3 days, the water was siphoned off, and the silt transferred to a half-gallon jar. The jar was then filled with water that had been associated with the sample and forwarded to the laboratory at Norris, Tennessee. When the percentage of silt in suspension was

very small, especially at low water stage, several collections were necessary to obtain enough silt for analysis. Frequently, several samples were combined to form a composite sample. Where a range of dates for sampling is shown in the tables, these represent the several dates on which the material making up the composite samples was collected.

The silt samples from the Mississippi River passes are composites taken at intervals through the vertical section of the channel, in several different, but not consecutive, months in 1938 and 1939, presumably at different levels of flow, in the course of regular measurements of the velocity and silt content of the river.

### Chemical determinations and methods of analyses

The determinations selected to develop agricultural significance were the percentages of the total and exchangeable bases, calcium, magnesium, and potassium (reported as CaO, MgO, and $K_2O$), the total phosphorus (reported as $P_2O_5$), and nitrogen. The determination of the percentage of exchangeable bases gives a proximate indication of the amount which is in active form and relatively available to plants, in distinction from the total. This distinction is not feasible for phosphorus and nitrogen, for which only the totals are reported.

In general, the procedure used in the analysis of the silt was, in principle, that prescribed by the Association of Official Agricultural Chemists for the analysis of soils, but with appropriate modifications. In the analysis of water the procedure for calcium and magnesium was that outlined in "Standard Methods of Water Analysis," (1) and for potassium a procedure recommended by Dr. W. H. MacIntire, chemist of the Tennessee Agricultural Experiment Station.

The total bases were determined by the fusion method, to bring the nutrients into solution, followed by accepted procedure of analysis.

The total phosphorus and nitrogen were determined from strong acid digestions of the sample, followed by regular analytical procedure. The exchangeable bases were determined by steam digestion of the sample, with a normal ammonium chloride solution, and subsequent analysis of the solution for the selected nutrients.

Analyses of the stream water for nutrients in solution were limited to total calcium, magnesium, and potassium, as CaO, MgO, and $K_2O$. The content of phosphorus was not determined, since only a mere trace of this nutrient is found in solution. Nitrogen was omitted because the amount of this nutrient is so much affected by sewage waste in the streams as to preclude an accurate measure of loss from the soil.

### RESULTS OF SILT ANALYSES

#### Composition of silt

The average and the maximal and minimal range of composition[4] of the silt for the various nutrients at each location for approximately the full year 1939

[4] The name of the element is used in general in this paper to refer to the nutrients, even though in all cases except nitrogen the nutrients are reported in the conventional oxide form.

and for the first half year of 1940 are given in table 2. Since some of the individual samples, especially those taken at low flow when the silt content was meager, are made up of several collections to obtain enough material for analysis, these composites further increase the number of collections of material embodied in the averages and make the results all the more representative of the composition of the full range of silt material in the stream. The number of samples represented by separate analyses that make up the average is shown in column 2 of table 2. Composites are considered as single samples.

The most outstanding differences in composition of the silt at the several locations in the Tennessee River system are the relatively low content of total and exchangeable calcium in Hiwassee River and the relatively high content of phosphorus in the silt of Duck River at Hurricane Mills, together with only a slightly lower percentage in the Tennessee River at Johnsonville just below where Duck River enters.[5] In all other respects the composition of the silt is similar for each nutrient at the several locations. There are secondary differences in the average, and there is a range of percentage for each constituent at each location. This range as well as the average percentage is shown in table 2.

With some exceptions, the maximal percentage of both total and exchangeable bases at any location tends to be at least twice as large as the minimal at that location. This range is less for potassium than for calcium and magnesium.

On the lower Mississippi River the results in general are similar to those on the Tennessee River system.

*Year 1939 compared with 1940.* The percentages of both the total and the exchangeable bases at all locations average higher in 1940 than in 1939, with two or three exceptions. The most marked difference is in calcium, both total and exchangeable. Knoxville has a particularly high maximum of calcium in 1940. On the other hand, the percentages of phosphorus and nitrogen run about the same in the two periods, though more of the locations tend to run higher in 1939 than in 1940. These differences might be affected by the fact that the 1940 record is for only the first 6 months, whereas the 1939 record is for the full year.

*Exchangeable bases.* The relation of the percentage of exchangeable bases to the total bases present is shown in table 3. It is evident that a much larger percentage of the total of calcium than of magnesium is in exchangeable form, and that only a very small percentage of the potassium is in this form.

*Relation of level of flow of the stream to the composition of silt.* In general, the incidence of constituents in the silt was not found to be affected by the level of flow, although there may be exceptions. At Knoxville and at Chattanooga, for example, the total and exchangeable calcium rises slightly as the flow falls. Nitrogen also tends to be slightly higher at all locations as the flow falls. On the other hand, phosphorus in the silt in Duck River rises with the level of flow.

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[5] These percentages may be abnormally high at Hurricane Mills and Johnsonville because of sediment from phosphate ore washing operations in the Duck River basin, some of which finds its way into the drainage water. On the other hand, it is to be expected that the silt from this watershed would show a higher content of phosphorus than at the other locations, because of the relatively high proportion of soils of high phosphorus content in that basin.

## TABLE 2

### Chemical analyses of silt in percentages by locations

| RIVER LOCATIONS | TOTAL NUMBER SAMPLES | YEAR | TOTAL BASES | | | | | | EXCHANGEABLE BASES | | | | | | TOTAL | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | CaO Avg. | CaO Range | MgO Avg. | MgO Range | $K_2O$ Avg. | $K_2O$ Range | CaO Avg. | CaO Range | MgO Avg. | MgO Range | $K_2O$ Avg. | $K_2O$ Range | $P_2O_5$ Avg. | $P_2O_5$ Range | N Avg. | N Range |
| Powell near Arthur | 60 | 1939 | 1.11 | 0.560-1.88 | 0.800 | 0.523-1.08 | 1.95 | 1.03 -3.19 | 0.778 | 0.530-1.192 | 0.186 | 0.135-0.300 | 0.021 | 0.008-0.020 | 0.126 | 0.109-0.140 | 0.267 | 0.224-0.320 |
| | | 1940 | 0.858 | 0.504-1.38 | 0.881 | 0.652-1.14 | 1.95 | 0.762-2.30 | 0.783 | 0.441-1.125 | 0.165 | 0.058-0.288 | 0.021 | 0.016-0.026 | 0.123 | 0.114-0.136 | 0.239 | 0.200-0.296 |
| Clinch near Tazewell | 62 | 1939 | 1.037 | 0.605-1.73* | 0.982 | 0.778-1.16* | 3.76 | 3.24 -4.06* | 0.733 | 0.438-1.631 | 0.155 | 0.101-0.301 | 0.026 | 0.021+ * | 0.116 | 0.102-0.126 | 0.247 | 0.192-0.296 |
| | | 1940 | 1.151 | 0.818-1.78 | 0.970 | 0.643-1.09 | 3.76 | 3.35 -4.44 | 0.784 | 0.513-1.076 | 0.120 | 0.078-0.175 | 0.026 | 0.019-0.032 | 0.101 | 0.087-0.120 | 0.197 | 0.160-0.256 |
| Hiwassee at Murphy | 32 | 1939 | 0.401 | 0.269-0.504* | 0.818 | 0.431-1.15* | 1.80 | 1.08 -2.64* | 0.160 | 0.080-0.211 | 0.048 | 0.026-0.067 | 0.026 | 0.026+ * | 0.119 | 0.100-0.140 | 0.221 | 0.132-0.272 |
| Duck near Hurricane Mills† | 34 | 1939 | 1.53 | 0.121-1.79* | 0.926 | 0.818-1.02 | 1.54 | 1.00 -1.66* | 0.689 | 0.582-0.773 | 0.052 | 0.038-0.074 | 0.024 | ........ | 0.024 | 0.408-0.786 | 0.23 | 0.188-0.280 |
| | | 1940† | 1.93 | 1.34 -3.10 | 0.713 | 0.576-0.844 | 1.64 | 0.654-1.92 | 0.736 | 0.500-0.916 | 0.055 | 0.016-0.080 | 0.024 | 0.011-0.036 | 0.451 | 0.378-0.556 | 0.20 | 0.132-0.320 |
| Tennessee at Knoxville | 60 | 1939 | 0.848 | 0.638-1.06* | 0.982 | 0.627-1.24 | 2.29 | 1.98 -2.81* | 0.792 | 0.473-0.983 | 0.259 | 0.084-0.408 | 0.027 | 0.021-0.021* | 0.167 | 0.110-0.278 | 0.234 | 0.168-0.272 |
| | | 1940 | 2.07 | 0.188-2.71 | 1.55 | 1.05 -2.04 | 2.29 | 1.99 -2.43 | 1.773 | 1.07 -2.703 | 0.766 | 0.449-1.033 | 0.027 | 0.02 -0.052 | 0.155 | 0.128-0.196 | 0.256 | 0.216-0.376 |
| Tennessee at Chattanooga | 52 | 1939§ | 0.884 | 0.538-1.44* | 1.038 | 0.766-1.29* | 1.67 | 0.542-2.15* | 0.608 | 0.426-1.279 | 0.123 | 0.096-0.174 | 0.022 | 0.019-0.027* | 0.139 | 0.117-0.166 | 0.215 | 0.184-0.264 |
| | | 1940 | | | | | | | | | | | | | | | | |
| Tennessee near Johnsonville† | 34 | 1939 | 1.199 | 0.896-1.32* | 0.890 | 0.786-1.187* | 1.55 | 1.29 -1.84* | 0.574 | 0.480-0.708 | 0.066 | 0.045-0.061 | 0.028 | * | 0.476 | 0.348-0.559 | 0.239 | 0.176-0.320 |
| | | 1940† | 1.454 | 1.03 -1.99 | 0.700 | 0.608-0.884 | 1.55 | 1.09 -2.06 | 0.613 | 0.552-0.652 | 0.079 | 0.052-0.100 | 0.028 | 0.019-0.050 | 0.488 | 0.308-0.548 | 0.217 | 0.136-0.352 |
| Mississippi: South Pass | 8 | 1938-39 | 1.12 | 1.10-1.15 | 1.52 | 1.45-1.59 | 1.07 | 0.99-1.15 | 0.672 | 0.607-0.731 | 0.175 | 0.171-0.180 | 0.038 | 0.029-0.047 | 0.115 | 0.068-0.145 | 0.237 | 0.216-0.256 |
| Southwest Pass | 8 | 1938-39 | 1.17 | 1.10-1.24* | 1.32 | 1.17-1.55* | 1.42 | 1.30-1.61* | 0.698 | 0.591-0.762 | 0.204 | 0.169-0.277 | 0.044 | 0.034-0.051 | 0.140 | 0.129-0.148 | 0.100 | 0.070-0.216 |
| Pass a l'Outre | 7 | 1938-39 | 1.14 | 1.09-1.24* | 1.46 | 1.06-1.89* | 1.66 | 1.24-2.38* | 0.705 | 0.569-0.833 | 0.235 | 0.180-0.353 | 0.042 | 0.031-0.053* | 0.136 | 0.130-0.151 | 0.151 | 0.086-0.256 |

* Incomplete record.

† Probably contains washings from phosphate ore.

‡ Some samples in 1939.

§ Average of 2 years.

This may indicate an increase in material from the phosphate ore washings in such periods of high flow.

### Annual quantity of nutrients in silt

The records of the Hydraulic Data Division show the total volume of flow of the streams at each location for the period covered by the samplings and the approximate silt content of the drainage water, from which is calculated the total amount of silt carried for the period. The total quantity of each nutrient carried is calculated from the percentage compositions, reported in table 2, and the total quantity of silt for the corresponding location. Flow and silt load data for the Mississippi River have been compiled by the Hydraulic Data Division

### TABLE 3
*Percentage of bases in the silt in exchangeable form*

| LOCATION | CaO | | MgO | | K₂O | |
|---|---|---|---|---|---|---|
| | 1939 | 1940 | 1939 | 1940 | 1939 | 1940 |
| Powell...................... | 70.0 | 91.0 | 21.6 | 18.7 | 1.08 | 1.08 |
| Clinch...................... | 70.5 | 68.0 | 15.8 | 12.4 | 0.69 | 0.69 |
| Hiwassee.................... | 40.0 | .... | 5.87 | .... | 1.44 | .... |
| Duck....................... | 45.0 | 38.2 | 5.62 | 7.7 | 1.56 | 1.56 |
| Knoxville................... | 92.5 | 86.0 | 26.4 | 49.5 | 1.18 | 1.18 |
| Chattanooga................ | 69.0 | .... | 11.85 | .... | 1.33 | .... |
| Johnsonville............... | 47.7 | 42.2 | 7.42 | 10.4 | 1.81 | 1.81 |
| Average.................. | 62.1 | 65.1 | 13.51 | 19.7 | 1.30 | 1.26 |
| Mississippi River | | | | | | |
| South Pass................. | 60.0 | .... | 11.5 | .... | 3.55 | .... |
| Southwest Pass............. | 59.7 | .... | 15.5 | .... | 3.1 | .... |
| Pass a l'Outre............. | 61.8 | .... | 16.1 | .... | 2.5 | .... |
| Average.................. | 60.5 | | 14.4 | | 3.05 | |

from published records (3, 4, 5) for an average year. To these data are applied analyses of samples of silt obtained from the army engineers, to get the quantity of the nutrients carried. The results of these calculations for the several locations are shown in table 4.

### Amount of silt and nutrients per acre of watershed

The total amount of silt and of each nutrient carried in a year at each location has been calculated to an average acre basis over the effective watershed. Data from the U. S. Census for 1940 permit the use of three measures in these calculations, namely:

(a) The total effective acreage of each watershed. The silt, however, does not come from the entire area. It might be considered to come from

(b) The open farmland (total farm area less forest area). But it does not come from the better sodland. Hence it comes mostly from

## TABLE 4

*Amount of plant nutrients and silt in tons at the several locations in 1939 and in first 6 months of 1940*

| LOCATION AND INCLUSION PERIOD | TOTAL SILT LOAD* | TOTAL BASES | | | EXCHANGEABLE BASES | | | TOTAL | |
|---|---|---|---|---|---|---|---|---|---|
| | | CaO | MgO | K₂O | CaO | MgO | K₂O | P₂O₅ | N |
| **Powell River at Arthur** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 174,200 | 1,934 | 1,498 | 3,397 | 1,355 | 324 | 37 | 219 | 465 |
| Jan., 1940–June, 1940 | 73,300 | 629 | 646 | 1,429 | 574 | 121 | 15 | 90 | 175 |
| **Clinch River at Tazewell, Tennessee** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 353,900 | 3,670 | 3,475 | 13,307 | 2,594 | 549 | 92 | 411 | 874 |
| Jan., 1940–June, 1940 | 120,600 | 1,388 | 1,170 | 4,535 | 946 | 145 | 31 | 122 | 238 |
| **Hiwassee River at Murphy, North Carolina** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 161,600 | 648 | 1,322 | 2,909 | 259 | 78 | 42 | 192 | 357 |
| **Duck River at Hurricane Mills, Tennessee** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 2,610,000† | 39,933 | 24,169 | 40,194 | 17,983 | 1,357 | 626 | 16,286† | 6,003 |
| Jan., 1940–June, 1940 | 1,195,500 | 23,083 | 8,525 | 18,411 | 8,799 | 658 | 287 | 5,392 | 2,391 |
| **Tennessee River at Knoxville, Tennessee** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 2,100,000 | 17,808 | 20,622 | 48,090 | 16,422 | 5,439 | 567 | 3,507 | 4,914 |
| Jan., 1940–June, 1940 | 596,400 | 12,345 | 9,244 | 13,658 | 10,574 | 4,568 | 161 | 924 | 1,527 |
| **Tennessee River at Chattanooga, Tenn.** | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 4,534,900‡ | 40,089 | 47,072 | 75,733 | 27,572 | 5,578 | 998 | 6,304 | 9,750 |
| Jan., 1940–June, 1940 | 476,100 | 4,209 | 4,942 | 7,951 | 2,895 | 586 | 105 | 662 | 1,024 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Tennessee River at Johnsonville | | | | | | | | | |
| Jan., 1939–Dec., 1939 | 7,322,600† | 87,798 | 65,171 | 113,500 | 42,032 | 4,833 | 2,050 | 34,856† | 17,501 |
| Jan., 1940–June, 1940 | 4,112,700 | 59,799 | 31,257 | 63,747 | 25,211 | 3,249 | 1,152 | 18,014 | 8,925 |
| Mississippi River: | | | | | | | | | |
| South Pass, Avg. year | 85,500,000 | 957,000 | 1,300,000 | 915,000 | 575,000 | 150,000 | 32,500 | 98,300 | 203,000 |
| Southwest Pass, Avg. year | 180,500,000 | 2,110,000 | 2,380,000 | 2,560,000 | 1,260,000 | 368,000 | 79,500 | 253,000 | 289,000 |
| Pass a L'Outre, Avg. year | 209,000,000 | 2,380,000 | 3,050,000 | 3,470,000 | 1,475,000 | 492,000 | 87,800 | 284,000 | 316,000 |
| Total carried by Mississippi River. Average year | 475,000,000§ | 5,447,000 | 6,730,000 | 6,945,000 | 3,310,000 | 1,010,000 | 199,800 | 635,300 | 808,000 |

* Silt loads in Tennessee River system have been estimated from runoff silt curves based on past records.

† Hurricane Mills and Johnsonville records probably include material from the washing of phosphate ore in the Central Basin, which increases the totals of all constituents and especially of phosphorus.

‡ The duplication of silt and nutrients at Knoxville in the Chattanooga record, and of Hurricane Mills in the Johnsonville record, is offset by the unrecorded silt collected in the reservoirs.

§ H. H. Bennett (2, p. 9) says that available data indicate that about 730 million tons of solid material annually is carried into the Gulf by the Mississippi River.

(c) The acreage in row crops, idle land, and land in farms other than that in forest, pasture, hay, and small grain.

The total area of the several watersheds is given in table 1. Where the stream passes through a reservoir, most, if not all, of the silt is deposited. The net effective area from which silt is derived, therefore, is the total area at the location minus the area of reservoir watersheds above that point; for example, the area above Chattanooga less Norris, Santeetlah, Parkville, and other reservoirs; Johnsonville less the area above the Pickwick Dam.

The data in table 5 show the losses of silt in tons and of nutrients in pounds per acre for the year 1939 by the three measures. For the Mississippi Valley only a rough estimate has been made of the (b) and (c) areas based on the proportion in nine states, selected at random, together with the Tennessee Valley. Each of these measures serves well to reduce the silt losses to a convenient approximate per-acre basis.

The loss of silt over the row crop, idle, and other areas ranged from 3.5 tons for the Tennessee River at Knoxville, and 6.65 tons at Chattanooga less Knoxville, to 10.8 for Duck River,[6] 13.0 tons at Johnsonville,[6] and 14.5 tons at Johnsonville less the Duck River drainage. In the Mississippi River it was 1.9 tons. Duck River was the only stream up to normal flow in 1939. In years of normal and high flow in the Valley the losses would be much above the figures shown in table 5. At the end of this section some further analysis is made of the relation of the quantity of material carried to the volume of flow. The relatively large amount of silt at Johnsonville is greater per acre than on Duck River at normal flow, or at any other location, which suggests that a substantial amount of the very fine material came through the reservoirs and was recorded at this station. This fact has been verified by supplementary calculations by the engineers of the Hydraulic Data Division. The quantity of silt primarily governs the amounts of the nutrients lost, which therefore appear correspondingly high at Johnsonville. This is brought out further in line 9 of table 5, where the quantities of material carried at Johnsonville are shown after deduction of those contributed by Duck River as measured at Hurricane Mills.

The data in this report indicate that very substantial quantities of silt and nutrients get away from the upland and are carried beyond reach into the reservoirs and into the Gulf of Mexico. No effort should be made, however, to evaluate these losses in terms of available fertilizer nutrients at commercial prices.

*Flow and silt content in test years compared with normal*

The Hydraulic Data Division's records of flow for a period of years indicate that, with the exception of Duck River, the flow in the test period was substantially below normal. The volume of flow at the several locations and the percentage of normal flow are given in table 6.

[6] Probably increased by material from washings of phosphate ore and very fine silt which come through the reservoirs.

## TABLE 5

*Approximate loss of silt, total Ca, Mg, K, P, and N, and exchangeable bases in the silt, per acre, by three measures of acreage in 1939*

| LOCATION | AREA IN WATERSHED (THOUSAND ACRES) | | | SILT LOAD (TONS PER ACRE) | | | TOTAL BASES (POUNDS PER ACRE) — CaO | | | MgO | | | K₂O | | | EXCHANGEABLE BASES (POUNDS PER ACRE) — CaO | | | MgO | | | K₂O | | | TOTAL (POUNDS PER ACRE) — P₂O₅ | | | N | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Total* | Open farm† | Row, idle other‡ | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other | Total | Open farm | Row, idle, other |
| 1. Powell River near Arthur | 437 | 175 | 41 | 0.40 | 1.00 | 4.25 | 8.9 | 22.1 | 94.3 | 6.86 | 17.1 | 73.0 | 15.5 | 38.8 | 165.7 | 6.2 | 15.5 | 66.0 | 1.48 | 3.7 | 15.8 | 0.17 | 0.42 | 1.80 | 1.02 | 2.5 | 10.7 | 2.12 | 5.3 | 22.7 |
| 2. Clinch River near Tazewell | 945 | 515 | 83.4 | 0.374 | 0.685 | 4.24 | 7.76 | 14.2 | 88.0 | 7.35 | 13.5 | 83.3 | 28.2 | 51.7 | 320.0 | 5.48 | 10.05 | 62.2 | 1.16 | 2.13 | 13.2 | 0.19 | 0.36 | 2.21 | 0.87 | 1.60 | 9.86 | 1.85 | 3.4 | 21.0 |
| 3. Hiwassee River, Murphy | 270 | 51.3 | 22 | 0.60 | 3.15 | 7.35 | 4.80 | 25.2 | 59.0 | 9.80 | 51.6 | 120.0 | 21.6 | 113.0 | 264.5 | 1.92 | 10.10 | 23.6 | 0.58 | 3.04 | 7.10 | 0.31 | 1.63 | 3.81 | 1.42 | 7.5 | 17.4 | 2.65 | 13.9 | 32.4 |
| 4. Duck River,§ Hurricane Mills | 1,650 | 883 | 241 | 1.58 | 2.95 | 10.8 | 48.4 | 90.3 | 331.0 | 29.3 | 54.7 | 200.0 | 48.7 | 91.0 | 334.0 | 21.8 | 40.7 | 149.0 | 1.65 | 3.07 | 11.30 | 0.76 | 1.42 | 5.20 | 19.8 | 37.0 | 135.0 | 7.30 | 13.6 | 50.0 |
| 5. Tennessee River, Knoxville | 5,720 | 2,802 | 600 | 0.367 | 0.75 | 3.50 | 6.25 | 12.7 | 59.5 | 7.22 | 14.7 | 69.0 | 16.8 | 34.2 | 160.0 | 5.75 | 11.7 | 54.9 | 1.90 | 3.87 | 18.15 | 0.20 | 0.41 | 1.89 | 1.23 | 2.50 | 11.7 | 1.72 | 3.5 | 16.4 |
| 6. Chattanooga | 8,780 | 3,850 | 966 | 0.516 | 1.18 | 4.70 | 9.15 | 20.8 | 83.0 | 10.7 | 24.5 | 97.5 | 17.3 | 39.4 | 157.0 | 6.29 | 14.3 | 57.0 | 1.27 | 2.90 | 11.60 | 0.23 | 0.52 | 2.07 | 1.44 | 3.28 | 13.1 | 2.22 | 5.1 | 20.2 |
| 7. Chattanooga less Knoxville | 3,060 | 1,048 | 366 | 0.795 | 2.32 | 6.65 | 14.6 | 42.5 | 122.0 | 17.3 | 50.5 | 144.4 | 18.1 | 52.8 | 151.0 | 7.3 | 21.3 | 61.0 | 0.09 | 0.27 | 0.76 | 0.28 | 0.82 | 2.36 | 1.83 | 5.35 | 15.3 | 3.16 | 9.2 | 26.4 |
| 8. Johnsonville§ below Pickwick | 3,660 | 1,623 | 565 | 2.00 | 4.50 | 13.00 | 48.0 | 108.2 | 311.0 | 35.6 | 80.4 | 231.0 | 62.0 | 140.0 | 401.0 | 23.0 | 51.8 | 149.0 | 2.04 | 4.59 | 17.1 | 1.12 | 2.52 | 7.26 | 19.0 | 43.0 | 123.4 | 9.6 | 21.6 | 62.0 |
| 9. Johnsonville§ below Pickwick less Duck | 2,010 | 740 | 324 | 2.35 | 6.37 | 14.5 | 47.6 | 129.0 | 296.0 | 40.8 | 111.0 | 253.0 | 73.0 | 198.0 | 453.0 | 24.0 | 65.0 | 148.0 | 3.46 | 9.40 | 21.4 | 1.42 | 3.85 | 8.8 | 18.5 | 50.2 | 114.6 | 11.42 | 31.1 | 71.0 |
| Mean‖ Mississippi River, Total Three Passes | 798,000 | 530,000¶ (66.5%) | 250,000¶ (31%) | 0.51 | 1.58 | 5.20 | 8.5 | 23.3 | 84.6 | 9.7 | 29.5 | 97.9 | 20.0 | 58.1 | 212.2 | 5.3 | 13.7 | 53.5 | 1.04 | 2.6 | 11.0 | 0.23 | 0.73 | 2.41 | 1.27 | 3.9 | 13.0 | 2.30 | 7.1 | 23.8 |
|  |  |  |  | 0.60 | 0.90 | 1.90 | 13.6 | 20.5 | 43.6 | 16.9 | 25.4 | 53.8 | 17.4 | 26.2 | 55.6 | 8.3 | 12.5 | 26.5 | 2.53 | 3.81 | 8.07 | 0.50 | 0.75 | 1.60 | 1.59 | 2.40 | 5.08 | 2.03 | 3.05 | 6.46 |

\* Total area of effective watershed in thousand acres. Reservoir watershed areas above station have been deducted.

† Open farm area includes all area in farms not in forest.

‡ Row crop, idle, and other land in farms, except hay, pasture, and small grains and woodland: Census 1940.

§ All data from Duck River and Johnsonville locations are omitted from means because of the probable effect of phosphate ore washings and silt from above Pickwick Dam.

‖ Mean of lines 1, 2, 3, 5, 7.

¶ Based upon an approximate percentage of the total area, determined from the rough proportion of 9 states and the Tennessee Valley in these groups by the Census of 1940. On this basis, open farm areas equals 66.5%, and row crop, idle, and other farm area equal 31%.

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It is known that the amount of silt carried by a stream usually increases with the volume of flow, but the silt carried may increase at a much faster rate than the volume of flow; that is, the silt content per unit of volume increases with the volume of flow. Hence, it may be said that at all locations, except Duck River and to a less extent in Tennessee River at Johnsonville, the volume of the silt and therefore of the nutrients carried in the test period was much below normal and still farther below what it is in years of highest flow.

Futhermore, it should be noted that although the farm test-demonstration operations and other methods designed to reduce losses from the soil by erosion had started in 1935, they were far from having attained their full effects, and from extension to all farms, when samples were taken for this study.

The quantity of phosphorus ($P_2O_5$) carried at each location each year from 1935 to 1939 inclusive, as calculated from the quantity of silt and its average

TABLE 6

*Average flow in 1939 and normal flow at the several locations*

| STATION | 1939 AVERAGE FLOW | PERCENTAGE OF NORMAL FLOW | NORMAL FLOW |
|---|---|---|---|
| | *cfs** | | *cfs* |
| Powell River near Arthur | 954 | 78 | 1,222 |
| Clinch River near Tazewell | 1,658 | 79 | 2,100 |
| Hiwassee River at Murphy | 817 | 85 | 963 |
| Duck River near Hurricane Mills | 4,506 | 115 | 3,930 |
| Tennessee River at Knoxville | 9,661 | 72 | 13,450 |
| Tennessee River near Chattanooga | 30,670 | 80 | 38,400 |
| Tennessee River near Johnsonville | 62,350 | 98 | 63,500 |

\* *cfs* = cubic feet per second.

analysis in 1939, and the relative flow for each year, using 1939 as 100, are shown in table 7.

Two facts are apparent from these data. First, the quantity of phosphorus carried does not invariably increase with the volume of flow, as is indicated by sags in some years of higher flow. It might be inferred that this is related to difference in the intensity characteristics of the rainfall for particular years. Sags appear for five locations: Powell, Hiwassee, Duck, Chattanooga, and Johnsonville, in 1937. Sags also appear in 1935 in Clinch and Duck Rivers. Secondly, the relative quantity of phosphorus, and hence also of silt carried, differ very greatly between streams, irrespective of the volume of flow. In Duck River the quantity of phosphorus increased very little with increase in annual flow. This may be due to the high proportion of land in sod and also to the less average slope of the land in that watershed. On the other hand, in Hiwassee River and in Tennessee River at Knoxville and Chattanooga there was a very large increase in amount of phosphorus with increase in volume of flow.

## BASES IN THE DRAINAGE WATER

Total bases in solution were determined in the water collected with the silt samples. As has been mentioned, phosphorus was not determined because only a trace is carried in the drainage water. Nitrogen was omitted because the amount is affected greatly by sewage and industrial waste discharged into the streams. Inspection of the analyses indicates that the calcium and magnesium also may be affected at some periods by industrial wastes. This should be taken into account in interpretating the analyses.

TABLE 7

*Relation of volume of flow to normal, and the actual and relative quantity of phosphorus ($P_2O_5$) at each location 1935 to 1939, using 1939 yield as 100*

| YEAR | POWELL RIVER | | | CLINCK RIVER | | | HIWASSEE RIVER | | | DUCK RIVWE | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Percentage of normal flow | $P_2O_5$ | Relative yield | Percentage of normal flow | $P_2O_5$ | Relative yield | Percentage of normal flow | $P_2O_5$ | Relative yield | Percentage of normal flow | $P_2O_5$ | Relative yield |
| | | tons | | | tons | | | tons | | | tons | |
| 1935 | 92 | 427 | 195 | 82 | 683 | 166 | 71 | 99 | 52 | 94 | 9,664 | 59 |
| 1936 | 97 | 478 | 218 | 85 | 881 | 214 | 110 | 680 | 354 | 81 | 9,665 | 59 |
| 1937 | 101 | 393 | 179 | 93 | 519 | 126 | 95 | 261 | 136 | 127 | 11,961 | 73 |
| 1938 | 92 | 214 | 98 | 100 | 435 | 106 | 93 | 391 | 204 | 84 | 13,393 | 82 |
| 1939 | 78 | 219 | 100 | 79 | 411 | 100 | 85 | 192 | 100 | 115 | 16,286 | 100 |

*Tennessee River*

| YEAR | KNOXVILLE | | | CHATTANOOGA | | | JOHNSONVILLE | | |
|---|---|---|---|---|---|---|---|---|---|
| | Percentage of normal flow | $P_2O_5$ | Relative yield | Percentage of normal flow | $P_2O_5$ | Relative yield | Percentage of normal flow | $P_2O_5$ | Relative yield |
| | | tons | | | tons | | | tons | |
| 1935 | 104 | 8,692 | 247 | 93 | 12,993 | 206 | 98 | 39,611 | 114 |
| 1936 | 119 | 11,451 | 327 | 102 | 16,989 | 270 | 100 | 53,015 | 152 |
| 1937 | 100 | 5,344 | 152 | 99 | 8,950 | 142 | 107 | 37,650 | 108 |
| 1938 | 87 | 3,701 | 106 | 89 | 7,417 | 118 | 88 | 32,333 | 93 |
| 1939 | 72 | 3,507 | 100 | 80 | 6,304 | 100 | 98 | 34,856 | 100 |

## *Average analyses*

The straight average analysis at each location and the average, weighted by the volume of flow by periods, are given in table 8, together with the mean volume of flow of the stream.

The water in the streams is from both the surface runoff and underground flow in variant proportions. If not contaminated by industrial and city wastes, it should reflect roughly the composition of the soil solution, except that water that passes through the soil moves mostly in the larger crevices and channels and relatively little in the minute spaces in which plant rootlets feed and where the solution in intimate contact with the soil particles is much more concentrated.

These figures serve, however, to indicate the losses of nutrients in solution in the streams.

In these analyses the results for potassium probably are less affected by extraneous conditions than are the results for calcium and magnesium.

TABLE 8

*Flow of streams and bases in solution at the several locations*

| LOCATION | AVERAGE FLOW | TOTAL BASES | | | NUMBER OF SAMPLES |
|---|---|---|---|---|---|
| | | CaO | MgO | K₂O | |
| | cfs* | p.p.m.† | p.p.m. | p.p.m. | |
| *Powell River near Arthur, Tenn.* | | | | | |
| Straight average...................... | 3,262 | 32.0 | 11.0 | 1.36 | 32 |
| Weighted average‡.................... | | 32.8 | 9.25 | 1.34 | |
| *Clinch River near Tazewell, Tenn.* | | | | | |
| Straight average...................... | 4,398 | 38.1 | 10.6 | 1.34 | 34 |
| Weighted average.................... | | 36.0 | 8.53 | 1.22 | |
| *Hiwassee River at Murphy, N. C.* | | | | | |
| Straight average...................... | 1,578 | 4.15 | 2.85 | 1.22 | 9 |
| Weighted average.................... | | 4.53 | 2.09 | 1.07 | |
| *Duck River near Hurricane Mills, Tenn.* | | | | | |
| Straight average...................... | 9,006 | 44.8 | 5.32 | 1.45 | 20 |
| Weighted average.................... | | 43.2 | 3.98 | 2.05 | |
| *Tennessee River at Knoxville, Tenn.* | | | | | |
| Straight average...................... | 11,875 | 44.4 | 7.69 | 1.49 | 29 |
| Weighted average.................... | | 40.6 | 6.77 | 1.24 | |
| *Tennessee River at Chattanooga, Tenn.* | | | | | |
| Straight average...................... | 11,900 | 40.2 | 6.7 | 1.55 | 29 |
| Weighted average.................... | | 41.9 | 6.86 | 1.53 | |
| *Tennessee River near Johnsonville, Tenn.* | | | | | |
| Straight average...................... | 60,260 | 36.1 | 5.56 | 1.43 | 21 |
| Weighted average.................... | | 34.3 | 5.8 | 1.12 | |

* Cubic feet per second.

† p.p.m. = parts per million parts of water.

‡ Weighted by the volume of flow for each sampling period.

The content of calcium and magnesium trends downward slightly at all locations as the level of flow increases. The content of calcium is less uniform than that of the other two bases.

### Quantity of bases in solution

From the actual flow, its relation to normal flow, the normal volume of flow shown in table 6, and the normal annual flow at each location, the normal quantity of the bases carried in solution, based on analyses for 1939 and 1940, were calculated and are shown in table 9.

From these quantities and the area of each watershed, the approximate average annual volume of flow per acre and the pounds of each base in solution per acre of total area of watershed were calculated and are shown in table 10.

TABLE 9

*Normal annual flow and total amount of bases in solution, based on weighted average composition for periods of analysis*

| LOCATION | TOTAL FLOW IN NORMAL YEAR | BASES | | |
|---|---|---|---|---|
| | | CaO | MgO | $K_2O$ |
| | million cu. ft. | tons | tons | tons |
| Powell River............................. | 38,600 | 39,600 | 11,200 | 1,620 |
| Clinch River............................. | 66,200 | 74,400 | 17,600 | 2,530 |
| Hiwassee River........................... | 30,400 | 4,310 | 2,000 | 1,020 |
| Duck River.............................. | 124,000 | 167,200 | 15,420 | 7,950 |
| Tennessee River—Knoxville................ | 425,000 | 540,000 | 90,000 | 16,400 |
| Tennessee River—Chattanooga.............. | 1,210,000 | 1,580,000 | 259,500 | 57,800 |
| Tennessee River—Johnsonville.............. | 2,000,000 | 2,141,000 | 365,000 | 70,000 |

TABLE 10

*Approximate normal average volume of flow and bases in solution per acre of total watershed*

| LOCATION | AREA OF WATERSHED | AVERAGE ANNUAL FLOW PER ACRE WATERSHED | | BASES CARRIED IN SOLUTION PER ACRE PER YEAR | | |
|---|---|---|---|---|---|---|
| | | | Equivalent* rainfall | CaO | MgO | $K_2O$ |
| | acres | cu. ft. | inches | lbs. | lbs. | lbs. |
| Powell River............... | 438,000 | 88,100 | 24.3 | 180 | 51 | 7.4 |
| Clinch River............... | 944,000 | 70,100 | 19.3 | 158 | 37 | 5.4 |
| Hiwassee River............ | 270,000 | 112,600 | 31.0 | 32 | 15 | 7.6 |
| Duck River................ | 1,645,000 | 75,400 | 20.7 | 203 | 19 | 9.7 |
| Tennessee River: | | | | | | |
| Knoxville................ | 5,700,000 | 74,500 | 20.6 | 188 | 32 | 5.8 |
| Chattanooga.............. | 13,700,000 | 88,300 | 24.3 | 232 | 38 | 8.4 |
| Johnsonville.............. | 24,600,000 | 81,000 | 22.3 | 174 | 30 | 5.7 |
| Average................ | | 84,286 | 23.2 | 167 | 31.7 | 7.1 |

\* The normal average annual rainfall over the Valley ranges from 80 inches in the southeastern mountain region to 40 inches over much of the lower elevations.

The loss of bases per inch of runoff averaged for all locations was 7.21 pounds of calcium, 1.37 pounds of magnesium, and 0.31 pound of potassium.

COMPARISON OF QUANTITY OF BASES LOST IN SILT AND IN SOLUTION

The comparison of the quantity of bases carried in the silt and in solution per year, per acre of watershed, is shown in table 11, on the basis of the mean quantity for all the locations.

The quantities in solution are for normal flow, whereas the quantities in the silt are for 1939, when all but Duck River were below normal flow. The silt losses come largely from the surface soil, while the material in solution may come more largely from the depths of the soil formation.

TABLE 11

*Comparison of the mean quantity of bases per acre per year carried in silt and solution*

| BASES | SILT IN 1939 MEASURED BY AREA | | | | | | SOLUTION NORMAL FLOW TOTAL WATER-SHED |
| | Total effective water-shed | | Effective open farm-land | | Row crop and other land in farms | | |
| | Total | Exchang. | Total | Exchang. | Total | Exchang. | |
| | lbs. | lbs. | lbs. | lbs. | lbs. | lbs. | lbs. |
| Calcium (CaO)............ | 8.5 | 5.3 | 23.3 | 13.7 | 84.6 | 53.5 | 164 |
| Magnesium (MgO)......... | 9.7 | 1.04 | 29.5 | 2.6 | 97.9 | 11.08 | 35 |
| Potassium ($K_2O$)........... | 20.0 | 0.23 | 58.1 | 0.73 | 212.2 | 2.41 | 7.3 |
| Phosphorus ($P_2O_5$)......... | 1.27 | .... | 3.9 | ..... | 13.0 | ..... | ..... |
| Nitrogen.................. | 2.30 | .... | 7.1 | ..... | 23.8 | ..... | ..... |

## SUMMARY

Samples of water and silt were collected at frequent intervals during a year and a half at seven locations in the Tennessee River system, three on tributary streams and four on the main river.

Chemical analyses were made of each collection of silt for the full period for total and exchangeable calcium, magnesium, and potassium, and total phosphorus and nitrogen. Analyses of the water associated with the silt were made for nearly a full year for total calcium, magnesium, and potassium. Samples of silt also were obtained from the lower Mississippi River, and corresponding analyses made.

The total quantities of silt and of the several nutrients carried for the year 1939 were calculated from the records of stream flow and silt content and are expressed as quantities per acre of the effective watershed at each location. Three measures of acreage were used: Total, open farm area, and row crop and other relatively exposed land area. When the row crop and other acreage measure was used, these quantities per acre averaged 5.20 tons of silt, 84.6 pounds of calcium, 97.9 pounds of magnesium, 212.2 pounds of potassium, 13.0 pounds of phosphorus, all expressed as oxides, and 23.8 pounds of nitrogen.

The quantity of the three bases as oxides carried in solution, at normal flow at each location for a full year, averaged per acre of watershed, 167.0 pounds of calcium, 31.7 pounds of magnesium, and 7.1 pounds of potassium.

All streams except Duck River were below normal flow in the test period. Records of the annual flow and silt content at each location for 5 years from 1935 indicated that in general the quantities of silt and nutrients increased sharply with the volume of flow, with the exception of one year, probably because of the characteristics of the rainfall and the surface of the watershed.

The composition of the silt varied little, if any, with the level of flow, and watersheds differed chiefly in the content of calcium and phosphorus.

Corresponding data on the composition of silt and losses per acre are presented also for the lower Mississippi River.

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# HYDROGEN-ION CONCENTRATION OF THE IMPORTANT SOILS OF THE UNITED STATES IN RELATION TO OTHER PROFILE CHARACTERISTICS: III. INTRAZONAL SOILS

ERNEST H. BAILEY[1]

*U. S. Department of Agriculture*

The hydrogen-ion concentrations of the zonal soils were discussed in two earlier papers (1, 2). The present paper deals with the intrazonal soils, which include the halomorphic, hydromorphic, and calcimorphic soils.

## HALOMORPHIC SOILS

The halomorphic soils consist of the great soil groups: solonchaks, solonetz, and solodi.

### Solonchaks

Table 18 shows some of the profile characteristics and the hydrogen-ion concentrations of the solonchaks (27, 28, 63). Three series, the Pond, Land, and Lahontan soils (8, 9, 42, 53, 67, 70), were selected to represent this group. They occur in the sierozem desert and red desert soil regions. The pH values of the six profiles range from 7.3 to 10.3. These values agree substantially with those obtained by other investigators (27, 37, 60), but the range is wider. Three of the profiles are more alkaline than pH 9.0, and one has pH values above 10.0. There appears to be no uniformity as to where in these profiles the most alkaline or the least alkaline horizons occur.

The Pond profiles (8, 42) are the most alkaline of the solonchak soils (Table 18). Two horizons of one profile have a pH of 10.3. These soils are probably developing into solonetz soils. Their high pH values indicate a high content of sodium or potassium carbonates.

The Land profiles (9, 70) are very variable in alkalinity. One profile has a pH of 9.9 in one of its layers, which is higher than any horizon in one of the Pond profiles, while the other profile has the lowest pH values of the solonchaks. One horizon has a pH value of 7.3.

The two Lahontan profiles (53, 67) are the most uniform in pH values. They average the lowest in pH of the solonchaks.

### Solonetz soils

Table 19 shows some of the physical properties and pH values of the solonetz soils (27, 28, 38, 63). Three series were selected to represent this group of soils: the Beadle from the chernozem soil zone, the Phillips from the chestnut and

## TABLE 18
*Solonchaks*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 302 | *Pond clay* "Puff spot," Wasco area, Calif. | 0–1 | Grayish brown granular light clay loam, no surface crust | 8.3 |
| | | 1–3 | Faint brownish gray silty clay loam, large clods which break up easily | 9.4 |
| | | 3–16 | Grayish brown light clay, breaks into large clods that are easily broken up | 9.7 |
| | | 16–50 | Bright yellowish brown heavy clay, granular structure and very soft in profile | 9.6 |
| | | 50–60 | Dull brown heavy clay loam, compact faint streaks of lime | 9.8 |
| 303 | *Pond clay loam* Wasco area, Calif. | 0–3 | Dark grayish brown clay loam, surface laminated, finely vesicular beneath | 9.7 |
| | | 3–12 | Dark grayish brown clay loam with a large lumpy structure, chunks finely vesicular | 10.3 |
| | | 12–22 | Dark yellowish brown clay with a little grit, massive and very compact, a few vertical seams of white lime | 10.3 |
| | | 22–36 | Light gray sandy clay in loose lumps which are extremely compact, vertical white streaks of lime | 9.3 |
| | | 36–40 | Light yellowish gray clay loam, friable granular structure, massive in profile | 9.3 |
| 305 | *Land loam* Pahrenegat Valley area, Nev. | 0–½ | Thin alkali crust. Light brownish gray loam with alkali efflorescence on upper surface | 9.0 |
| | | ½–4 | Light loam, forming a brown granular mulch full of salt | 9.1 |
| | | 4–20 | Firm, soft, cloddy pale brown silty clay loam flecked with white | 9.1 |
| | | 20–26 | Loose light brownish gray loamy sand | 8.8 |
| | | 26–72 | Thin alternating strata of weak brown silt loam with white flecks and mellow pale brown fine sandy loam | 9.9 |
| 306 | *Land silty clay loam* Moapa Valley area, Nev. | 0–¼ | Crust of pale brown silt loam | 7.6 |
| | | ¼–1½ | Mulch of pale brown granulated silt loam | 7.5 |
| | | 1½–5 | Light brown slightly compact silt loam | 7.3 |
| | | 5–13 | Light brown, slightly mottled with pale brown and black, heavy silty clay loam; salt content very high | 7.5 |
| | | 13–45 | Loose brownish gray fine sand | 8.8 |
| | | 45–72 | Compact light brown silty clay slightly mottled with light gray; salt crystals visible | 8.4 |

TABLE 18—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 307 | *Lahontan clay loam* | 0-1 | Surface crust, very light brownish gray | 8.6 |
| | Newlands project, Nev. | 1-8 | Granular subsurface mulch, light brownish gray clay loam | 8.1 |
| | | 8-36 | Compact clay, weak brown | 7.8 |
| 308 | Newlands project, Nev. | 0-1 | Crust, light gray | 8.7 |
| | | 1-8 | Mulch, light brown clay loam | 7.6 |
| | | 8-36 | Compact weak brown clay | 7.8 |

brown soil zones, and the Tubac from the red desert soil zone (17, 18, 65, 66). The pH values of the solums of the six profiles studied vary from 5.3 to 9.0, and those of their C horizons from 7.6 to 8.4. This range is almost identical with that obtained by other investigators (6, 27, 32, 37, 51, 54, 61) and is considerably less than that of the solonchak profiles (table 18). Theoretically, the solonchak soils are supposed to be less alkaline than the solonetz soils, at least in the compact horizons. This seeming discrepancy may be explained by the fact that these solonetz profiles are all more or less solodized (27, 28).

Of the solonetz profiles studied, all but one show a higher pH in the dense columnar horizon than in the more friable upper horizons, and four of the six profiles show a more alkaline reaction in the compact than in the C horizon. With the exception, however, of one profile, in which the upper part of the columnar layer is slightly acid, all of the compact layers are neutral or above.

Of the profiles studied, upper horizons of the Beadle average the most acid, but the surface horizon of one of the Phillips profiles has the lowest pH, 5.3. On the other hand, another Phillips profile has the most alkaline surface horizon, with a pH value of 8.2 at the surface and 8.8 in the compact horizon immediately beneath. The Beadle profile from Brown County, South Dakota, has the most alkaline compact horizon, with a pH of 8.1 in the upper part and 9.0 in the lower.

### Solodi soils

The writer was unable to obtain any solodi profiles. This group appears to be very transitory and hence exceedingly rare.

#### HYDROMORPHIC SOILS

The hydromorphic soils include the following great soil groups: Wiesenböden, half-bog soils, ground-water podzols, and planosols.

### Wiesenböden

Table 20 shows some of the morphological characteristics and the hydrogen-ion concentrations of the Wiesenböden profiles (63). Two series, the Webster and the Clyde, were selected to represent this group of soils. The two are very similar in appearance. The pH values of the profiles range from 5.8 to 8.3.

### TABLE 19
*Solonetz soils*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 309 | *Beadle silt loam* McCook Co., S. Dak. | 0–9 | Grayish brown silt loam | 6.3 |
| | | 9–21 | Compact horizon. Black or dark brown plastic clay loam | 7.9 |
| | | 21–42 | C Olive-brown clay loam mottled with gray and brown; calcareous | 7.8 |
| 311 | Brown Co., S. Dak. | 0–3 | Brown silt loam | 5.5 |
| | | 3–8 | Dark brown silt loam | 5.5 |
| | | 8–10 | Gray silty clay loam | 7.0 |
| | | 10–17 | Compact horizon. Black, dense, slowly pervious clay | 8.1 |
| | | 17–21 | Compact horizon. Brownish yellow silty clay loam with lime streaks | 9.0 |
| | | 21–30 | $C_1$ Yellow calcareous silty clay | 8.0 |
| | | 30–36 | $C_2$ Yellow drab mottled silty clay | 8.1 |
| 313 | *Phillips loam* "Slick spot" Northern Plains of Montana | 0–¼ | Light gray fine sandy and gravelly mulch | 7.8 |
| | | ¼–4 | Hardpan. Hard, compact, dull drab-brown loam; calcareous | 8.3 |
| | | 4–10 | Compact horizon. Compact light brown loam, not so hard as layer above; calcareous | 8.5 |
| | | 10–22 | Compact horizon. Compact; hard, gray, mottled brown clay loam; calcareous | 8.1 |
| | | 22–36 | C Light brown with some gray mottling, compact but easily friable silt loam | 7.9 |
| 314 | Northern Plains of Montana | 0–6 | Light brown loose loam | 5.3 |
| | | 6–10 | Compact horizon. Lighter brown compact cubical-structured loam | 6.3 |
| | | 10–17 | Compact horizon. Slightly dark grayish brown compact, hard cubical-structured sandy clay loam | 8.4 |
| | | 17–36 | C Light grayish-brown compact loam; calcareous; white lime areas scattered throughout | 8.4 |
| 315 | "Slick spot," Northern Plains of Montana | 0–½ | Gray silty to fine sandy loam mulch | 8.2 |
| | | ½–6 | Compact, light brown coarse heavy loam, cubical structure, friable, calcareous | 8.8 |
| | | 6–14 | Hardpan. Dull dark brown very compact silty clay loam; white lime and alkali areas | 8.0 |
| | | 14–36 | C Dull dark brown very compact silty clay loam-parent drift | 7.6 |

TABLE 19—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 317 | *Tubac gravelly sandy loam* | 0–5 | Moderate brown gravelly sandy loam, slightly granular; noncalcareous | 7.4 |
| | Nogales area, Ariz. | 5–12 | Compact horizon. Reddish brown noncalcareous compact clay, columnar structure | 7.8 |
| | | 12–20 | Compact horizon. Rich to light brown clay, compact columnar structure, slightly calcareous | 8.7 |
| | | 20–36 | Compact horizon. Light brown silt loam, highly calcareous, streaked with gray lime, somewhat columnar structure | 8.6 |
| | | 36–44 | $C_1$ Very light brown silt loam, compact, very calcareous, lime-streaked | 7.8 |
| | | 44–72 | $C_2$ Very pale brown gravelly sandy loam, very calcareous and compact, very heavily cemented in places | 8.1 |

This finding agrees very closely with the results obtained by other investigators on this group of soils, with the exception of Mattson and Gustafsson, who reported a range of pH from 4.1 to 5.1 on a Wiesenböden profile (3, 12, 39). The pH values of the solums of both soils tend to become higher with depth.

The Webster soils occur chiefly in the glaciated prairie regions of Iowa (36, 58). The pH of these two profiles ranges from 5.8 to 8.3. One of the profiles is medium acid in its surface horizons. The hydrogen-ion concentrations of these soils are very similar to those of the Clarion series (2, table 16), which have developed on similar parent material.

The Clyde series has developed in both the prairie and the gray-brown podzolic regions (44, 57). The pH varies from 5.9 to 6.8. This averages considerably lower than that of the Webster. The surface has a pH similar to that of the Carrington, with which it is closely associated in the prairie region, but the subsoil of the Clyde is much less acid (2, table 16). The Miami, which developed on the same parent material as the Clyde and with which the Clyde is closely associated in the gray-podzolic regions, has a similar pH range, but the Miami solums are most acid in the $A_2$ and B horizons, whereas the Clyde solums are most acid at the surface and become less acid with depth (2, table 12).

### Half-bog soils

Four series were studied as representative of the half-bog soils (63). They are the Brookston from the gray-brown podzolic soil regions, the Portsmouth from the gray-brown podzolic and the red and yellow podzolic soil regions, and the Coxville and the Bladen from the red and yellow podzolic soil regions. The pH values of these soils are extremely variable, depending on the nature of the parent material and the character of the surrounding upland soils.

The Brookston soils (15, 46) have developed on parent materials similar to

those of the Miami, Clyde, and Webster series. They are closely associated with the Miami and the Clyde series. The pH range is from 6.2 to 8.2 (table 21).

TABLE 20

*Wiesböden*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 319 | *Webster silty clay loam* Calhoun Co., Iowa | 0–8 | Very dark brown silty clay loam | 5.8 |
| | | 8–18 | Dark brown granular silty clay | 6.4 |
| | | 18–28 | Dark brown silty clay | 7.0 |
| | | 28–40 | Gray silty material—upper layer of lime concentration | 8.0 |
| | | 40–50 | Friable silty material, mottled dull gray and pale yellow | 8.2 |
| | | 50–60 | Gray mixed with yellow and yellowish brown silty material | 7.9 |
| | | 60–70 | Parent material. Gray, plastic silty clay with much grit and some coarse material —glacial till | 7.9 |
| 320 | Hancock Co., Iowa | 0–2 | Black silty clay loam—grass roots | 7.5 |
| | | 2–14 | Black silty clay loam to silty clay | 7.7 |
| | | 14–18 | Dark grayish brown silty clay, faintly mottled with gray | 7.8 |
| | | 18–27 | Dull gray silty clay, mottled with dark grayish brown; calcareous | 8.1 |
| | | 27–37 | Dull gray silty clay; heavy lime nodules | 8.2 |
| | | 37–51 | Dull gray silty clay, mottled with brown, some sand | 8.3 |
| | | 51+ | Yellow to yellowish brown clay, highly streaked with gray—glacial till | 8.1 |
| 324 | *Clyde silt loam* Howard Co., Iowa | 0–10 | Dark brown to black silt loam | 6.2 |
| | | 10–14 | Brown heavy clay loam breaking into coarse granules | 5.9 |
| | | 14–17 | Dark gray mixture of sand and clay | 6.1 |
| | | 17+ | Gray and brown mixture of sand, gravel, and clay—glacial till | 6.0 |
| 328 | *Clyde silty clay loam* Wells Co., Ind. | 0–6 | Black granular silty clay loam, heavier with depth | 6.2 |
| | | 6–16 | Very dark drab, heavy silt loam with rusty brown spots | 6.7 |
| | | 16–36 | Drab, silty clay loam grading into lighter-colored clay | 6.8 |

This is similar to that of the Webster soils but considerably more alkaline than that of the Clyde profiles studied (tables 20 and 21). The pH differs from that of the Miami series in being more uniform throughout the profile and in not having so high a degree of acidity as the former soil in some of its lower A and

## TABLE 21
### *Half-bog soils*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 330 | *Brookston silty clay loam* Blackford Co., Ind. | 0–4 | Very dark brownish gray silty clay loam | 6.2 |
| | | 4–20 | Dark grayish brown silty clay loam | 6.8 |
| | | 20–40 | Mottled yellow, gray, and rust-brown sticky very plastic clay | 7.0 |
| | | 40–70 | Mottled, light gray, yellow, and grayish yellow sticky plastic silty clay loam | 7.1 |
| | | 70–90 | Buried soil. Very dark grayish brown silty clay loam | 7.1 |
| | | 90–130 | Mottled yellow and bluish gray clay loam | 7.1 |
| | | 130–160 | Blue-gray, very sticky and plastic clay | 7.8 |
| | | 160–200 | Gray sticky plastic clay | 8.0 |
| 331 | *Brookston clay* Ottawa Co., Ohio | 0–2 | Very dark gray clay | 7.0 |
| | | 2–5 | Dark gray clay | 6.7 |
| | | 5–12 | Mottled dark gray and yellow clay | 7.0 |
| | | 12–23 | Gray clay, mottled with yellowish brown | 7.4 |
| | | 23–29 | Dull gray to rust-brown heavy clay loam | 8.0 |
| | | 29–36 | Dull gray and rust-brown mottled clay loam till | 8.1 |
| | | 36–42 | Dull gray and rust-brown calcareous clay loam till | 8.2 |
| 336 | *Portsmouth fine sandy loam* Lenoir Co., N. C. | 0–15 | Dark gray fine sandy loam | 4.1 |
| | | 15–35 | Gray fine sandy loam | 4.3 |
| | | 50–70 | Mottled gray and yellow fine sandy clay | 4.4 |
| 338 | *Portsmouth loam* Caroline Co., Md. | 0–5 | Brown loam | 4.1 |
| | | 5–14 | Black loam | 4.1 |
| | | 14–24 | Gray clay | 3.8 |
| | | 24–40 | Light gray sand | 4.1 |
| 339 | *Coxville very fine sandy loam* Jackson Co., Miss. | 0–6 | Nearly black very fine sandy loam | 4.6 |
| | | 6–12 | Pale yellow faintly mottled very fine sandy loam | 4.7 |
| | | 12–20 | Yellow finely mottled friable fine sandy clay loam | 4.6 |
| | | 20–30 | Mottled friable fine sandy clay loam | 4.7 |
| | | 30–40+ | Mottled plastic clay | 4.6 |
| 340 | Martin Co., N. C. | 0–4 | Gray loam to very fine sandy loam | 3.8 |
| | | 4–9 | Light gray heavy very fine sandy loam mottled with yellow | 4.2 |
| | | 9–22 | Steel gray heavy clay mottled with yellow and brownish yellow | 4.2 |
| | | 22–48 | Yellow and gray heavy plastic clay splotched with bright red | 4.5 |

TABLE 21—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 345 | *Bladen fine sandy loam* Carteret Co., N. C. | 0–5 | Dark gray heavy fine sandy loam | 3.6 |
| | | 5–17 | Gray heavy fine sandy loam | 4.2 |
| | | 17–48 | Gray heavy plastic clay mottled with ocherous yellow | 4.3 |
| 347 | *Bladen very fine sandy loam* Nancemond Co., Va. | 0–2 | Leaf litter | 3.8 |
| | | 2–5 | Deep steel gray very fine sandy loam | 3.9 |
| | | 5–10 | Gray very fine sandy loam | 4.2 |
| | | 10–36 | Gray, slightly plastic clay mottled with rust-brown | 4.5 |
| | | 36–62 | Gray plastic clay | 4.7 |

upper B horizons (2, table 12). It is similar to the Wiesenböden in showing a strong tendency to become increasingly alkaline with depth (table 20). One out of the two profiles is slightly acid in the surface horizon, the other one is neutral.

The Portsmouth, Coxville, and Bladen (12, 14, 26, 47, 48, 49, 69) series all have comparatively uniform low pH values throughout their profiles, a characteristic of many of the red and yellow podzolic soils (2, tables 13 and 14). The organic matter in the absence of lime develops strong acidity. These three soils have developed in poorly drained depressions in the coastal plain where not only is the parent material noncalcareous, but the surrounding upland soils are also noncalcareous.

The Portsmouth occurs in adjoining parts of the gray-brown podzolic and the red and yellow podzolic soil regions. In the gray-brown podzolic region the soils with which it is associated are the Collington, the Sassafras, and others of intermediate drainage conditions. In the yellow podzolic soil regions, Portsmouth soils are associated with the Norfolk and soils of intermediate drainage conditions. The pH values of the Portsmouth profile from the gray-brown podzolic soil regions are very similar to those of the Sassafras and Collington profiles (2, table 12), but the profile developed in the yellow podzolic region is slightly more acid than the Norfolk profiles, the chief upland soil of the region (2, table 14).

The Coxville and the Bladen series occur with the Norfolk soils, but have formed on different parent material. The pH ranges from 3.6 to 4.7.

### Ground-water podzols

Table 22 gives some of the morphological characteristics of the ground-water podzol (63) profiles and the pH values of their horizons. Three series were selected to represent this group: the Saugatuck (40, 64), from the podzol and gray-brown podzolic soil zones, and the Leon and St. Johns (16, 48), from the red and yellow and gray-brown podzolic soil zones. The Saugatuck occurs

chiefly in the podzol soil zone, and the Leon and St. Johns occur chiefly in the red and yellow podzolic soil zones.

The profiles of all of these soils are more or less acid throughout their solums (table 22). The pH values of their solums range from 3.7 to 5.2, and those of their C horizons from 4.4 to 6.0. These findings agree very well with the data

TABLE 22

*Ground-water podzols*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 351 | *Saugatuck sand* Menominee Co., Mich. | 2–0 | $A_0$ Dark brown forest litter and leaf mold | 4.4 |
| | | 0–13 | $A_2$ Whitish gray fine sand | 4.7 |
| | | 13–25 | $B_2$ Coffee-brown cemented fine sand | 4.8 |
| | | 25–38 | C Gray leached sand, water-saturated in lower part | 6.0 |
| 352 | Crawford Co., Mich. | 3–0 | $A_0$ Dark brown forest litter and leaf mold | 4.1 |
| | | 0–12 | $A_2$ Light gray sand | 4.4 |
| | | 12–21 | $B_2$ Brownish and rust-colored cemented sand | 4.9 |
| | | 21–33 | C Grayish wet sand | 5.5 |
| 353 | *Leon sand* Polk Co., Fla. | 0–5 | $A_1$ Gray sand | 4.4 |
| | | 5–21 | $A_2$ Very light gray sand | 5.2 |
| | | 21–30 | $B_2$ Hardpan. Very dark brown sand | 4.8 |
| | | 30–40 | $B_{21}$ Brown sand with dark brown stains | 5.1 |
| | | 40–80 | C Pale yellowish gray sand | 5.1 |
| 354 | *Leon fine sand* Brunswick Co., N. C. | 0–5 | $A_1$ Gray fine sand | 4.2 |
| | | 5–18 | $A_2$ Light gray to nearly white fine sand | 4.9 |
| | | 18–38 | $B_2$ Dark brown hardpan layer | 4.2 |
| | | 38+ | C Brownish gray wet sand | 4.4 |
| 355 | *St. Johns fine sand* Brunswick Co., N. C. | 0–2 | $A_0$ Brown, peaty mass of roots, leaves, and twigs | 3.7 |
| | | 2–13 | $A_1$ Nearly black fine sand—considerable organic matter | 3.8 |
| | | 13–18 | $A_2$ Light gray loose fine sand | 4.3 |
| | | 18–32 | $B_2$ Dark brown hardpan layer | 3.9 |
| | | 32+ | $C_2$ Brownish gray wet sand | 4.6 |

reported on this group by Hearn (24) and by Till (62). The appearance of the profiles is very similar to that of the podzols (2, tables 10 and 12).

Both of the Saugatuck profiles have the greatest acidity at the surface, and the acidity gradually decreases with depth. In this respect, the profiles are very similar to the podzol profiles (2, table 10).

The Leon and the St. Johns series have both developed on poorly drained coastal plain deposits in New Jersey, Delaware, Maryland, North Carolina, South Carolina, Georgia, and Florida. The C horizons of both soils are very

slightly less acid than the solums, with the exception of the $A_2$ horizons in the profiles. In both the Leon and St. Johns profiles, the greatest acidity occurs in the humus and organic hardpan layers (table 22).

The St. Johns profile is slightly more acid than the Leon profiles. The profiles of these two serves average slightly more acid than those of the gray-brown and red and yellow podzolic soils with which they are associated (2, tables 12, 13, 14).

## Planosols

Planosols (63) belonging to four subgroups were selected for study: those developed in the chernozem, in the reddish chestnut, in the Prairie, and in the podzolic soil zones (1, fig. 1).

*Planosols in the chernozem zone.* Table 23 shows some of the morphological characteristics of the planosol profiles from the chernozem zone and their hydrogen-ion concentrations. The Crete series was selected to represent this subgroup (23, 50).

The pH values of the horizons above the lime zone vary from 5.3 to 7.7, and those of the lime horizons and below, from 7.2 to 8.3. These results are very similar to those reported by Brown, Rice, and Byers on this subgroup (6). Of the three profiles studied, one has horizons above the lime zone that are strongly acid and two have some upper horizons that are of medium acidity. Hence, the upper layers average more acid than do those of the chernozems (1, table 2). Like the chernozems, the lime layer is always more alkaline than any of the horizons above it. The compact layers have hydrogen-ion concentration intermediate between the horizons above and the lime horizon below it. The acid horizons of the Crete soils, together with some of the A horizons of the solonetz soils in the chernozem and chestnut soil regions, are the most acid horizons in profiles showing a zone of lime accumulation.

*Planosols in the reddish chestnut soil zone.* Table 24 shows some of the morphological characteristics of the planosol profiles in in the reddish chestnut soil zone (1, fig. 1) and their hydrogen-ion concentrations. The Foard series (19, 20, 21) was selected to represent this subgroup.

The pH values of the horizons above the lime range from 7.2 to 8.7, and those of the lime horizons and below, from 7.6 to 9.0. This is considerably more alkaline than that of the planosols in the chernozem region (table 23). They also have a higher pH than the chernozem soils studied (1, table 2) and higher than the reddish chestnut profiles, with which this series is associated (1, table 4). Some horizons above the lime in one profile are neutral and the upper layers of two profiles are mildly alkaline. One profile has horizons more alkaline than pH 8.5. These highly alkaline horizons occur in the lower part of the compact horizon and in the lime horizon. In two profiles the compact horizon is intermediate in pH between the horizons above and below it. This agrees with the profiles of the planosols so far studied (table 23). One profile is slightly less alkaline in the lime horizon than in the lower part of the compact horizon.

*Planosols in the prairie region.* Table 25 gives some of the profile characteri-

istics and hydrogen-ion concentrations of the planosols in the prairie region (1, fig. 1). Four series were selected to represent this subgroup: the Grundy, Putnam, Cherokee, and Parsons (5, 13, 30, 33, 34, 35, 45).

TABLE 23

*Planosols in the chernozem zone*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 362 | *Crete silt loam* Clay Co., Neb. | 0–1 | Dust mulch. Dark grayish brown friable silt loam | 6.2 |
| | | 1–7 | Very dark grayish brown to dark brown laminated layer, friable silt loam | 5.9 |
| | | 7–21 | Very dark grayish brown granular silt loam | 6.1 |
| | | 21–31 | Compact horizon. Dark brown heavy silt loam | 6.9 |
| | | 31–36 | Compact horizon. Grayish brown silty clay loam | 7.7 |
| | | 36–39 | Lime horizon. Gray friable silt loam | 8.2 |
| | | 39–59 | Lime horizon. Loose lighter gray silt loam | 8.3 |
| | | 59–120 | Lime horizon. Loose light gray silt loess | 8.1 |
| 363 | Saline Co., Neb. | 0–½ | Dust mulch. Grayish brown silt loam | 5.7 |
| | | ½–8 | Very dark grayish brown silt loam—laminated layer | 5.3 |
| | | 8–20 | Very dark grayish brown laminated layer | 5.3 |
| | | 20–32 | Claypan. Dark grayish brown silty clay loam | 6.3 |
| | | 32–40 | Claypan. Yellowish brown silty clay loam | 6.7 |
| | | 40–60 | Lime horizon. Grayish yellow silt loam | 7.8 |
| | | 60–75 | Yellow loess, many iron stains; no lime | 7.2 |
| 364 | Clay Co., Kans. | 0–10 | Dark grayish brown silt loam, laminated gray between layers | 5.6 |
| | | 10–15 | More brown in color and less laminated silt loam | 5.7 |
| | | 15–25 | Compact horizon. Rich brown to yellowish brown silty clay loam, strongly columnar | 6.1 |
| | | 25–30 | Compact horizon. Heavy silty clay, columnar; greenish brown to greenish yellow | 6.2 |
| | | 30–50 | Lime horizon. Light brown friable silty clay loam | 7.7 |
| | | 50–84 | Roughly columnar, dark reddish brown silt loam | 7.8 |

The pH values of the solums of these profiles vary from 4.9 to 7.8, and those of their C horizons, from 6.2 to 8.0. These results are similar to the data of Norton and Bray (43), but the former have a greater range. They have the same range as those of the associated prairie soils (2, table 16). Of the eight profiles, five show the highest pH in the C horizon. In the other profiles,

the C horizon has virtually the same reaction as the lower layers of the B horizon (table 25). All are slightly acid to strongly acid at the surface. Of the eight profiles selected, the claypan layers of six are intermediate in reaction between the horizons above and below, one has the same pH as the A horizon, and one

## TABLE 24

*Planosols in the reddish chestnut soil zone*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 365 | *Foard silt loam* | 0–4 | Very dark reddish brown silt loam | 7.7 |
| | Kiowa Co., Okla. | 4–12 | Compact horizon. Dark reddish brown stiff clay loam | 7.4 |
| | | 12–25 | Compact horizon. Yellow stiff clay | 7.5 |
| | | 25–36 | Compact horizon. Yellow-brown stiff clay | 8.5 |
| | | 36–66 | Compact horizon. Darker yellow-brown stiff clay | 7.9 |
| | | 66–78 | Lime horizon. Reddish brown friable clay | 7.8 |
| | | 78–96+ | Red friable clay | 8.2 |
| 366 | Tillman Co., Okla. | 0–3 | Very dark reddish brown laminated silt loam | 7.8 |
| | | 3–10 | Compact horizon. Very dark reddish brown to black silt loam, nut structure | 8.0 |
| | | 10–18 | Compact horizon. Very dark reddish to yellowish brown clay, large nut structure | 8.7 |
| | | 18–36 | Lime horizon. Yellow brown friable clay | 9.0 |
| | | 36–50 | Yellowish brown clay with a reddish tint | 8.0 |
| | | 50–74 | Red clay | 8.3 |
| 367 | Greer Co., Okla. | 0–1 | Very dark reddish brown friable laminated silt loam | 7.2 |
| | | 1–6 | Compact horizon. Dark reddish brown cloddy silty clay loam | 7.7 |
| | | 6–12 | Compact horizon. Very dark reddish brown stiff cloddy silty clay loam | 7.6 |
| | | 12–18 | Compact horizon. Dark reddish brown stiff clay | 7.3 |
| | | 18–38 | Lime horizon. Friable pink clay with soft lime lumps | 8.0 |
| | | 38–76 | Lime horizon. Friable yellowish red clay with lime lumps | 7.7 |
| | | 76–120 | Parent material. Red clay of the Permian red beds | 7.6 |

has the same pH as the C horizon. Four of the eight profiles are most acid at the surface and gradually decrease in acidity downward, one is most acid in the lower A, and three have the greatest acidity in the lower A and upper B horizons.

The Cherokee profiles average the most acid of the four series studied, but they appear to have developed from material lower in bases than the other soils,

TABLE 25

*Planosols in the prairie region*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 370 | *Grundy silt loam* Monroe Co., Iowa | 0–1½ | A₁ Dark grayish brown granular silt loam | 6.4 |
| | | 1½–12 | A₂ Dark grayish brown silt loam, slightly lighter in color than A₁ | 6.6 |
| | | 12–18 | A₃ Grayish brown coarse granular heavy silt loam | 5.9 |
| | | 18–26 | B₁ Yellowish brown coarse granular light silty clay loam | 5.8 |
| | | 26–29 | B₂ Claypan. Dark drab heavy silty clay mottled gray and brown | 5.8 |
| | | 29–40 | B₂₁ Claypan. Dark gray compact silty clay loam mottled with yellowish brown | 6.2 |
| | | 40–63 | B₃ Gray light silty clay loam mottled with rusty brown | 6.5 |
| | | 63+ | C Parent material. Gray silt loam mottled with brown | 7.2 |
| 371 | Union Co., Iowa | 0–2 | A₁ Dark grayish brown silt loam, grass root mat | 6.1 |
| | | 2–4 | A₂ Very dark grayish brown silt loam very finely granular | 5.7 |
| | | 4–13 | A₃ Nearly black heavy silt loam | 5.7 |
| | | 13–23 | B₁ Very dark brown silty clay | 6.0 |
| | | 23–30 | B₂ Claypan. Black plastic silty clay slightly mottled with dark gray | 6.3 |
| | | 30–39 | B₂₁ Claypan. Mottled gray and brown plastic clay | 6.7 |
| | | 39–46 | B₂₂ Mottled gray and brown silty clay | 7.2 |
| | | 46–58 | B₃ Brown silty clay | 7.2 |
| | | 58–70 | C₁ Gray friable silty clay | 7.3 |
| | | 70–90 | C₂ Gray friable silty clay streaked with white | 7.9 |
| | | 90–107 | C₃ Brown silty clay streaked with grayish white | 8.0 |
| 373 | *Putnam silt loam* Montgomery Co., Ill. | 0–6 | A₁ Grayish brown friable silt loam | 5.7 |
| | | 6–12 | A₂ Very light gray floury silt loam | 5.7 |
| | | 12–16 | B₁ Claypan. Dark gray heavy, tough impervious clay mottled with brown | 6.1 |
| | | 16–22 | B₂ Claypan. Heavy mottled dark gray and brown stiff impervious clay | 6.9 |
| | | 22–30 | B₂₁ Claypan. Heavy mottled light gray and brown clay. Not quite so heavy as B₂ | 7.3 |
| | | 30–40 | B₃ Claypan. Gray and yellow heavy silty clay loam | 7.7 |
| | | 40–49 | C₁ Gray and yellow light silty clay loam | 7.8 |
| | | 49–62 | C₂ Gray and yellowish brown heavy silt loam | 7.7 |

TABLE 25—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 376 | Marion Co., Mo. | 0–7 | $A_1$ Grayish brown smooth friable silt loam | 5.4 |
| | | 7–15 | $A_2$ Ashy gray, floury silt loam containing rust-brown soft iron concretions | 4.9 |
| | | 15–25 | $B_2$ Claypan. Heavy plastic impervious clay, mottled with gray, dark gray-brown, and black | 4.9 |
| | | 25–45 | $B_{21}$ Claypan. Dark gray clay, not quite so plastic and impervious as $B_2$ | 5.6 |
| | | 45–55 | C Gray silt loam mottled with brown and yellowish brown | 6.6 |
| 378 | *Cherokee silt loam* Cooper Co., Missouri | 0–6 | $A_1$ Grayish brown silt loam | 6.1 |
| | | 6–20 | $A_2$ Light grayish brown silt loam | 5.7 |
| | | 20–26 | $B_2$ Claypan. Dark brown tough very heavy clay, breaks into cubical blocks | 5.7 |
| | | 26–40 | C Mottled gray and yellow heavy and compact clay with pieces of shale | 6.2 |
| 379 | Vernon Co., Missouri | 0–7 | $A_1$ Grayish brown silt loam | 5.4 |
| | | 7–15 | $A_2$ Light gray silt loam | 5.3 |
| | | 15–20 | $B_2$ Claypan. Dark gray stiff impervious clay | 5.6 |
| | | 36–45 | C Loose parent material. Olive-gray clay loam mottled with brown; pieces of shale | 6.2 |
| 383 | *Parsons silt loam* Woodson Co., Kans. | 0–5 | $A_1$ Dark gray silt loam | 5.3 |
| | | 5–10 | $A_2$ Light gray silt loam | 5.6 |
| | | 10–16 | $B_1$ Dark grayish brown clay tinged with red | 6.4 |
| | | 16–30 | $B_2$ Claypan. Yellowish gray dense clay | 7.6 |
| | | 30–40 | $B_3$ Claypan. Light grayish yellow clay | 7.8 |
| | | 40–60 | C Ashen yellow disintegrated shale | 7.7 |
| 384 | *Parsons silty clay loam* Marion Co., Kans. | 0–7 | $A_1$ Dark grayish brown slity clay loam | 5.4 |
| | | 7–9 | $B_1$ Dark gray to grayish brown heavy silty clay loam to silty clay, granular | 5.5 |
| | | 9–24 | $B_2$ Claypan. Grayish black dense heavy clay with numerous brown specks | 6.9 |
| | | 24–34 | $B_3$ Claypan. Dark grayish brown heavy dense clay | 6.9 |
| | | 34–45 | $B_4$ Olive-gray clay, contains numerous semihard very dark brown pellets | 7.8 |
| | | 45–90 | $B_5$ Light brown rather friable clay, becomes more friable with depth | 7.5 |
| | | 90–100 | C Olive-gray to light greenish yellow shaly material, rather silty | 7.5 |

as their C horizons have a lower pH than those of the other three soils. The Putnam averages the next most acid, followed by the Parsons. The degree of compaction in the B horizon does not appear to affect the reaction of the profile, as the Putnam, which comes from the same parent material as the Grundy and has a much more impervious and dense claypan, averages only slightly more acid than the latter soil. There is not a great deal of difference in reaction among the four soils.

*Planosols in the podzolic soil zones.* Table 26 gives some of the profile characteristics of the planosols in the podzolic soil zones and the pH values of their horizons. Four series were selected to represent these soils. They are the Caneadea and Crosby (7, 25, 56, 59), in the gray-brown podzolic soil region, and the Lebanon and Dickson, which occur in adjacent parts of the gray-brown Podzolic and the red and yellow podzolic soil regions (22, 29, 31, 55).

The pH values of these profiles range from 4.1 to 8.2. This is a trifle more acid than the podzolic soils of the region with which they are associated (2, tables 12, 13, 14). The pH values of the solums of these profiles range from 4.1 to 7.8, and those of their C horizons, from 4.1 to 8.2. These results agree very closely with those obtained by other investigators (4, 11, 43). The reaction of the C horizons depends upon the lime content of the parent material. With the exception of one of the Crosby profiles, all of these soils are slightly to very strongly acid at the surface. The reactions of the profiles are most heterogeneous but there is a strong tendency for the profiles to be the most acid in either the lower A or the B horizon.

The Lebanon (31, 55) have the most acid solums of the four soils studied, and the Crosby averages the least acid. As the Crosby (7, 59) has developed from the most alkaline parent material, this influence may still be affecting the solum. Soils of this series show a decided tendency to develop a higher acidity in their solums than the Miami soils that are derived from the same parent material (2, table 12). The Crosby, like the Miami, is neutral to mildly alkaline in the lower part of the B horizon. Like the Crosby, the other planosols in the podzolic soil zones show a slight tendency to develop more acid solums than the corresponding zonal soils.

### *Calcimorphic-rendzina soils*

The Houston series (1, fig. 1; 10, 41, 68) was selected as representative of the calcimorphic-rendzina soils (38, 63). Table 27 shows some of the morphological characteristics and pH values of the rendzina profiles.

The pH values of the solums of these profiles vary from 7.6 to 8.6, and those of their C horizons from 7.8 to 8.8. These results are very similar to those reported by de'Sigmond (52) and by Liatsikas (37), except that those in table 27 show a greater range. The three profiles average more alkaline than either the prairie or the chernozem soils (1, table 2; 2, tables 16, 17). There is no horizon of lime accumulation, but the high calcium carbonate content of the soft chalky parent material dominates the entire profile, so that it resembles the prairie and chernozem profiles even in the regions of the red and yellow podzolic soils.

TABLE 26
*Planosols in the podzolic soil zones*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | | pH |
|---|---|---|---|---|---|
| | | *inches* | | | |
| 386 | *Caneadea silt loam* Lake Co., Ohio | 0–4 | $A_1$ | Dark gray silt loam | 6.1 |
| | | 4–6 | $A_2$ | Gray silt loam | 5.9 |
| | | 6–10 | $A_3$ | Gray silt loam faintly mottled with yellowish brown. | 5.9 |
| | | 10–20 | $B_2$ | Compact horizon. Mottled light gray and yellowish brown finely granular silty clay loam | 5.9 |
| | | 20–36 | $B_{21}$ | Compact horizon. Finely granular gray silty clay mottled with yellowish brown, iron concretions | 6.1 |
| | | 36–46 | C | Mottled gray and yellowish brown silty clay | 7.0 |
| 388 | *Caneadea silty clay loam* Tioga Co., Pa. | 0–1 | $A_1$ | Grayish yellow silty clay loam | 5.1 |
| | | 1–5 | $A_2$ | Mottled gray, grayish yellow, and yellow silty clay loam | 4.7 |
| | | 5–18 | $B_1$ | Compact horizon. Mottled gray and brownish gray rusty brown clay loam | 5.1 |
| | | 18–30 | $B_2$ | Compact horizon. Mottled gray, brownish gray, and rusty brown clay | 5.3 |
| | | 30–168 | $C_1$ | Stratified yellowish gray silt loam to grayish brown clay | 7.0 |
| | | 168–240 | $C_2$ | Dull olive clay | 7.5 |
| | | 240–260 | $C_3$ | Grayish yellow silty clay | 8.1 |
| 391 | *Crosby silt loam* Randolph Co., Ind. | 1–0 | $A_0$ | Mull—oak, maple, and hickory leaves | 6.3 |
| | | 0–1 | $A_1$ | Very dark brown silt loam | 5.8 |
| | | 1–4 | $A_2$ | Dark grayish brown silt loam | 5.5 |
| | | 4–8 | $A_3$ | Grayish yellow silt loam | 4.5 |
| | | 8–12 | $B_1$ | Compact horizon. Mottled yellow and gray heavy silty clay loam | 4.8 |
| | | 12–18 | $B_2$ | Compact horizon. Dark yellowish brown silty clay loam | 4.9 |
| | | 18–24 | $B_{21}$ | Compact horizon. Dark yellowish brown silty clay loam mottled with gray | 5.9 |
| | | 24–30 | $B_3$ | Compact horizon. Calcareous dark yellowish brown heavy silty clay loam | 7.8 |
| | | 30+ | C | Yellowish and grayish yellow calcareous glacial till | 8.2 |
| 392 | Blackford Co., Indiana | 1–0 | $A_0$ | Dark brown leaf mold | 7.6 |
| | | 0–4 | $A_1$ | Dark grayish brown silt loam | 7.6 |
| | | 4–10 | $A_2$ | Pale grayish yellow silt loam, slightly more yellow with depth | 4.7 |
| | | 10–18 | $B_2$ | Compact horizon. Granular silty clay loam mottled with yellowish brown and light gray | 4.9 |
| | | 18–30 | $B_3$ | Compact horizon. Mottled light and dark brown heavy silty clay loam, coarsely granular | 6.9 |
| | | 30+ | C | Yellow and gray heavy calcareous glacial till | 8.2 |

TABLE 26—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 395 | *Lebanon silt loam* <br> Phelps Co., Missouri | 0–6 | A Grayish brown friable silt loam | 4.5 |
| | | 6–11 | $B_1$ Brownish yellow silty clay loam to chocolate-brown tough clay | 4.2 |
| | | 11–24 | $B_2$ Mottled bluish gray and pale yellow silty clay loam, more friable than $B_1$ | 4.2 |
| | | 24–30 | $B_3$ Claypan. Mottled red and gray chert fragments cemented together into a dense clay | 4.4 |
| | | 30–48 | $B_{31}$ Claypan. Dense red clay with some gray mottling containing chert fragments | 4.1 |
| | | 48+ | C Reddish brown very friable cherty silty clay loam | 4.1 |
| 396 | Phelps Co., Missouri | 0–1 | $A_1$ Dark gray floury silt loam | 4.9 |
| | | 1–3 | $A_2$ Ashy gray floury silt loam | 4.6 |
| | | 3–11 | $A_3$ Yellowish gray heavy silt loam with brown iron stains | 4.4 |
| | | 11–17 | $B_1$ Claypan. Heavy gray plastic silty clay loam with a little buff mottling | 4.5 |
| | | 17–34 | $B_{11}$ Claypan. Yellowish gray silty clay mottled with bluish gray | 4.3 |
| | | 34–44 | $B_2$ Claypan. Dense compact mass of gray silty clay mottled with buff. Small amount of chert. | 4.3 |
| | | 44–48 | C Reddish brown very friable cherty silty clay loam | 4.6 |
| 401 | *Dickson silt loam* <br> Lauderdale Co., Ala. | 0–¾ | $A_1$ Light gray floury silt loam | 5.4 |
| | | ¾–7 | $A_2$ Pale yellowish gray silt loam | 4.8 |
| | | 7–22 | $A_3$ Light yellow silt loam | 4.9 |
| | | 22–28 | $B_2$ Compact horizon. Mottled gray and brown heavy silty clay loam | 5.0 |
| | | 28–36 | $B_{21}$ Compact horizon. Mottled gray and brown heavy silty clay loam | 5.1 |
| | | 36–50 | $B_3$ Compact horizon. Mottled red, gray, and brown heavy silty clay loam | 5.1 |
| | | 50–65 | C Partly weathered red and gray silty clay and rotten chert | 5.1 |
| 402 | Dickson Co., Tenn. | 0–2 | $A_1$ Dark gray silt loam | 4.6 |
| | | 2–6 | $A_2$ Grayish brown silt loam | 5.2 |
| | | 6–18 | $B_1$ Compact horizon. Yellowish brown silty clay loam | 5.0 |
| | | 18–26 | $B_2$ Compact horizon. Yellow silty clay loam | 4.6 |
| | | 26–30 | $B_{21}$ Compact horizon. Yellow silty clay loam slightly streaked with gray | 4.8 |
| | | 30–36 | $B_3$ Compact horizon. Mottled gray, yellow, and brown cherty clay | 4.8 |
| | | 36–40 | C Red clay containing some chert fragments | 4.7 |

The pH and profile characteristics of the rendzinas stand out in sharp contrast to those of red and yellow podzolic soils (2, tables 13, 14).

### TABLE 27
*Rendzinas*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 403 | *Houston clay* | 0–2 | $A_1$ Almost black clay | 8.3 |
| | Bell Co., Tex. | 2–6 | $A_2$ Black clay | 8.4 |
| | | 6–22 | $A_3$ Rich brown clay | 8.4 |
| | | 22–40 | $B_1$ Brown limy clay | 8.4 |
| | | 40–60 | $B_2$ Yellowish limy clay | 8.6 |
| | | 60–70 | C Parent material. Creamy yellow marly clay | 8.8 |
| 404 | Dallas Co., Ala. | 0–6 | $A_1$ Very dark gray clay | 7.6 |
| | | 6–14 | $A_2$ Dark gray clay | 7.7 |
| | | 14–20 | $B_1$ Yellowish gray clay | 8.0 |
| | | 20–54 | $B_2$ Grayish yellow clay | 7.8 |
| | | 54–110 | C Mottled bright yellow and blue-gray clay | 7.8 |
| 407 | Sumter Co., Ala. | 0–4 | $A_1$ Black heavy plastic clay, dries out granular on exposed surface | 7.8 |
| | | 4–10 | $A_2$ Very dark gray to black plastic clay, lime modules present | 7.9 |
| | | 10–25 | $B_1$ Dark gray to very dark gray heavy plastic clay, lime nodules present | 8.0 |
| | | 25–36 | $B_2$ Dark olive-greenish gray, limy, heavy plastic clay, lime nodules present | 8.2 |
| | | 36–50 | $C_1$ Grayish dark yellow clay with an olive-green cast, plastic and sticky, lime nodules | 8.2 |
| | | 50–60 | $C_2$ Olive-green to grayish yellow calcareous clay with numerous hard lime nodules | 8.2 |

### SUMMARY

The solums of the solonchaks are the most alkaline of the profiles studied. They range from neutral to very strongly alkaline. This group appears to have no uniformity as to where in the profile the most alkaline or the least alkaline horizons occur.

The solums of the solonetz soils vary from strongly acid to strongly alkaline. Most of the solums show a higher pH in the dense columnar horizons than in the surface horizons. Two thirds of the profiles are more alkaline in the compact horizon than in the C horizon.

The solums of the Wiesenböden range from medium acid to strongly alkaline, and they show a tendency to increase in pH value with depth.

The profiles of the half-bog soils in regions where soils are high in lime and

where the parent material is also high in lime vary from slightly acid to strongly alkaline. The profiles of the half-bog soils in regions where soils are low in bases and where the parent material is also low in bases range from extremely acid to very strongly acid. The profiles of the half-bog soils formed on parent material high in lime have a general tendency to become more alkaline with depth, whereas the soils from regions low in bases tend to have the same pH throughout the profile.

The ground-water podzols range from extremely acid to strongly acid in their solums. They are the most acid in the A₁ and B horizons.

The reactions of the planosols strongly tend to be similar to those of the zonal soils with which they are associated. The planosols in the podzolic soil regions, however, tend to be slightly more acid than the corresponding zonal soils, the planosols in the chernozem soil zone tend to be more acid in the horizons above the lime than do the normal chernozems, and the planosols in the reddish chestnut region tend to be more alkaline in the horizons above the lime than do the normal reddish chestnut profiles.

The calcimorphic soils are represented by the rendzinas. The solums of this group range from midly alkaline to strongly alkaline. Apparently, the solums tend to have an alkaline reaction throughout.

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# BOOKS

*The Chemical Formulary.* Volume 7. Edited by H. BENNETT. Chemical Publishing Co., Inc., Brooklyn, New York, 1945. Pp. 474. Price $6.

As the title indicates, this is "a collection of valuable, timely, practical commercial formulae and recipes for making thousands of products in many fields of industry." The several chapters include adhesives, flavors and beverages, cosmetics and drug products, emulsions and colloids, farm and garden specialties, food products, inks and marking substances, skins—leather and fur, lubricants and oils, materials of construction, metals and alloys, paints and varnishes, paper, photography, polishes, pyrotechnics, plastics, soaps, and textiles and fibers. For the soil-plant scientist there are hydroponic formulas, cut-flower preservatives, grafting waxes, insecticides, fungicides, and weed-killers, as well as a great variety of other very useful information under the other headings.

*The Farmer's Last Frontier.* By FRED A. SHANNON. Farrar & Rinehart, Inc., New York, 1945. Pp. 434, illus. 28. Price, coll. ed. $3.75, trade ed. $5.

This is the fifth of nine volumes on "The Economic History of the United States." The third volume of this series was also concerned with agriculture, for the period 1815–1860. The author has not written a technical review of agriculture but has "tried to view the scene as the farmer saw it and to picture the farmer himself as he affected and was influenced by the world in which he lived." The 16 chapters deal with nature and the farmer, settlement in areas, the public domain, land and labor in the South, southern crops and problems, farm mechanization, expansion of prairie agriculture, special problems of prairie farmers, the Great-Plains farmer, marketing problems of the range country, specialized agriculture, governmental activity, the agrarian uprising, farmers' cooperatives, the farmer and the nation, and literature of the subject. The presentation is logical, thoughtful, and thought-provoking. Both those who live on and off the land will find it interesting and instructive. For the student, one of the most attractive features of the book is the last chapter with its review of the literature on the agriculture of the United States.

*Introduction to College Chemistry.* By WILLIAM McPHERSON, WILLIAM EDWARDS HENDERSON, W. CONRAD FERNELIUS, AND LAURENCE LARKEN QUILL. Ginn and Company, New York, 1942. Pp. 608, figs. 346. Price, $3.50.

As the title indicates, this, is a textbook for first-year students in chemistry. In it an attempt has been made to present a modern point of view without sacrificing any of the factual essentials. The authors introduce the electron concept early in the text and treat "water, air, the earth's crust, and salt as springboards for the introduction of many fundamental ideas." One chapter deals with soils, clay industries, and water supplies, and draws attention to a number of problems involved in the related industries. The text is essentially inorganic, but several chapters are devoted to hydrocarbons, carbohydrates, organic acids, and related compounds. A tremendous amount of work has gone

into the development of this elementary but comprehensive text. Teachers of freshman chemistry and persons in many other lines of endeavor will find the book of interest and value.

*Man and His Physical Universe.* By FRANK COVERT JEAN, EZRA CLARENCE HARRAH, AND FRED LOUIS HERMAN. Ginn and Company, New York, 1943. Pp. 608. Price, $3.50.

The purpose of this book is to "develop the understandings that will help the student locate himself in the universe, free him from superstition and prejudice, impress him with the importance of relying upon established truth in ordering his own life, and enable him to appreciate the careful, logical conclusions." It is hoped by this approach "to influence significantly the beliefs, philosophy, behavior, and attitudes of the future citizens of our democracy." Unit one has to do with the effect of man's knowledge of the cosmos on his thinking; unit two shows how the distinction between matter and energy was eliminated; unit three deals with organized energy and its properties; unit four outlines the uses to which energy is being put by man; unit five develops the science of meteorology as it affects mankind; and unit six considers the changing surface of the earth in relation to man's needs. In the hands of a capable and scientifically as well as educationally trained instructor, this book has highly important possibilities in fulfilling the purposes for which it is intended.

*The Soil Science Society of Florida Proceedings.* Volume 5-A. Interim meeting of the Society, Belle Glade and Clewiston, March 17–18, 1943. The Soil Science of Florida, R. V. Allison, Sec.-Treas., Gainesville. Pp. 187. Price, $1.

This report deals primarily with reclamation and soil conservation problems of the Florida Everglades. The several papers deal with surface waters, drainage, geological relationships, soil survey, vegetation, soil shrinkage due to drainage and oxidation, wildlife preservation, and a specific plan for the development of the area. Adoption of a resolution recommending the establishment and early development of the Everglades National Park is noted.

*Weeds of Lawn and Garden.* By JOHN M. FOGG, JR. The University of Pennsylvania Press, Philadelphia, 1945. Pp. 215, illus. 175. Price, $2.50.

This is a "handbook for eastern temperate North America." It is designed primarily for the amateur, but would be very useful to all those who have to do with the weed problem in practical agriculture. Each of 171 pages is devoted to a single weed, with a well-drawn illustration that makes it easy to identify the plant when studied in conjunction with the description immediately beneath. Suggestions for control are appended. The book is of pocket size, with a durable waterproof binding that makes it especially serviceable for field use.

THE EDITORS.

# INFLUENCE OF NITROGEN SOURCES IN THE FORMATION OF OXIDIZED AND REDUCED ORGANIC COMPOUNDS IN PLANTS

## A. V. VLADIMIROV

*Gedroiz Research Institute of Fertilizers, Agrotechnology, and Soil Science*

The researches of Prianishnikov and his associates (6, 7, 9), as well as those of investigators abroad (3, 5), have thrown sufficient light on problems of the metabolism of nitrogenous compounds and hydrocarbons in plants as affected by mineral nutrition. The effect of mineral nutrition on the metabolism of organic acids in plants has not been quite so thoroughly studied. The physiological role played by various substances in the processes involved in the formation of such economically valuable organic compounds as caoutchouc in koksaghiz, volatile oils in essential oil plants, and vitamins in vegetables likewise has received but little attention. For this reason, in the latest researches on the biochemical processes observable in the plant organism, the attention of this laboratory has been devoted primarily to the metabolism of organic acids and the changes that mineral nutrition brings about in the oxidation-reduction processes in plants, since the trend followed by these processes determines the nature of the storage of oxidized (organic acids) or reduced products (caoutchouc, pyrethrine, volatile oils, etc.).

Since 1938, this laboratory has been engaged in investigating the role of $NH_4^+$, $NO_2^-$, and $NO_3^-$, as well as that of potassium, magnesium, and certain other mineral substances, in the formation of oxidized and reduced organic compounds in plants. This article deals only with the data obtained on the effect of $NH_4^+$, $NO_2^-$, and $NO_3^-$ as sources of nitrogen.

An earlier publication on this same question (13) advanced the hypothesis that the stimulation of oxidation processes in plants should result in an increase in the organic acid content, especially that of citric acid. This hypothesis was based on the results of researches on the daily variations in the citric acid content of the leaves of the coarse variety of tobacco (*Nicotiana rustica*). These researches (12) established the fact that more citric acid was accumulated in the leaves during the nocturnal and early morning hours, *i.e.*, when the processes of respiration-oxidation are relatively predominant in the plant organism, than during midday.

The study of the effect of $NH_4^+$, $NO_2^-$, and $NO_3^-$ on the metabolism of organic acids in plants proceeded from the hypothesis that these forms of nitrogen should have markedly different effects on the oxidation-reduction processes in plants. This proposition was based on the work of Warburg (15), who observed in plants grown on nitrate, increased respiration with the production of additional $CO_2$ and the simultaneous reduction of nitrates to ammonia.

On the basis of the formula for the conversion of nitrogenous compounds in plants, long ago proposed by Prianishnikov ($NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ \rightarrow$ asparagine $\rightarrow$ amino acids $\rightarrow$ proteins), it was assumed that nitrates, being the oxi-

dized form of a nitrogenous compound, should, in the process of reduction to ammonia, oxidize other organic compounds found in the plant organism and convert them into organic acids (13). In the course of its conversion, ammonia, being the reduced form of a nitrogenous compound, cannot give rise to oxidizing processes in the plant organism, and for this reason, the organic acid content, especially that of citric and malic acids, must be lower in plants grown on ammonia than in those grown on nitrate.

## EXPERIMENTAL

To verify the foregoing hypotheses, a series of experiments were performed in 1938 and 1939 on the effect of nitrate and ammonia nitrogen on protein and carbohydrate metabolism and on the metabolism of organic acids in plants (14). The effect of $NH_4^+$, $NO_2^-$, and $NO_3^-$ on the formation of citric acid in plants also was studied in the laboratory with the aid of vacuum-infiltration. In these latter experiments the fourth and fifth leaves of the coarse variety of

TABLE 1

*Effect of $NH_4^+$ and $NO_3^-$ on the formation of citric acids in the leaves of N. rustica*

(1939 experiment)

| INFILTRATES | CITRIC ACID IN FRESH LEAVES | | | |
| --- | --- | --- | --- | --- |
| | 1st experiment, July 8, 9 a.m. | 2nd experiment, July 8, 11a.m. | 3rd experiment, July 13, 12 noon | 4th experiment, July 13, 2 p.m. |
| | *per cent* | *per cent* | *per cent* | *per cent* |
| H₂O............................ | 0.380 | 0.234 | 0.410 | 0.380 |
| (NH₄)₂SO₄........................ | 0.236 | 0.218 | 0.202 | 0.213 |
| H₂O............................ | 0.440 | 0.378 | 0.278 | 0.340 |
| NaNO₃........................... | .... | 0.489 | 0.452 | 0.570 |

the tobacco plant (*N. rustica*) were cut in half along the main vein. Distilled water was then infiltrated into one of the halves, and the solution being tested into the other. In all the experiments, 0.1 $N$ solutions were used for infiltration. After infiltration, the leaves were kept in a moist chamber under diffused light for 48 hours. The citric acid content of the leaves was then determined. The results are given in table 1.

Table 1 shows that the infiltration of a 0.1 $N$ solution of $NaNO_3$ into the leaves of *N. rustica* increases the citric acid content, whereas the infiltration of a 0.1 $N$ solution of $(NH_4)_2SO_4$ reduces it. Analogous results were obtained in experiments on *N. rustica* grown on sand cultures with continuous flow solutions.

These data demonstrate that ammonia nitrogen greatly diminishes the total acidity and the citric acid content of the leaves as compared with the nitrate form. This difference between ammonia and nitrate nitrogen became still more marked when their concentrations in the culture solutions were increased (table 2).

The data in table 2 show that the total titrable acidity and the citric acid content of the leaves of *N. rustica* diminish as the concentration of ammonium is increased from 10 to 40 mgm. of N per liter of solution, whereas with an increase in the concentration of nitrate nitrogen, the total acidity and citric acid content increase. With both nitrate and ammonia, an increase in the concentration of nitrogen is accompanied by a decrease in the sugar content.

On the basis of the foregoing data, we may make the following deduction: *nitrate nitrogen, being an oxidized form, creates in the plant organism conditions conducive to the intensification of the oxidation processes, in contradistinction to the ammonium or reduced form, which in the plant organism gives rise to conditions less favorable to the production and storage of organic acids in general and citric acid in particular.* This difference in the effect of $NH_4$ and $NO_3$ is more clearly manifested when the nitrogen concentration in the culture solution is increased.

TABLE 2

*Chemical composition of the leaves of N. rustica as affected by the concentration and form of nitrogen available*

(Data on dry-weight basis)

| CULTURE SOLUTION | | REDUCING SUGAR | TOTAL SUGAR | TOTAL ACIDITY | CITRIC ACID |
|---|---|---|---|---|---|
| Form of nitrogen | Nitrogen per liter solution | | | | |
| | *mgm.* | *per cent* | *per cent* | *m.e./100 gm.* | *per cent* |
| $NH_4$..................... | 40 | 0.38 | 0.46 | 141.2 | 0.546 |
| $NH_4$.................... | 10 | 0.77 | 2.15 | 181.7 | 1.154 |
| $NO_3$.................... | 40 | 0.46 | 0.95 | 270.9 | 3.240 |
| $NO_3$.................... | 10 | 3.87 | 5.45 | 259.3 | 1.219 |

Besides the ammonia and nitrate forms of nitrogen, of interest from the viewpoint of effect on the formation of organic acids in plants is the nitrite form as intermediate between nitrates and ammonia. To determine the nature of the effect of nitrites on the production and storage of citric acid in plants, a number of experiments were performed in 1939 with vacuum-infiltration, using the methods already described. The results of these experiments are presented in table 3.

Comparison of the data in the coupled cultures [$NaNO_3$ and $NaNO_2$, $(NH_4)_2SO_4$ and $NaNO_2$, and $NaNO_3$ and $(NH_4)_2SO_4$] shows that the citric acid content is higher in the $NaNO_3$ cultures than in the $(NH_4)_2SO_4$ cultures and that the $NaNO_2$ cultures occupy an intermediate position.

To study the effects of ammonia, nitrate, and nitrite nitrogen on the nitrogen and carbohydrate metabolism and on the metabolism of organic acids, which determine the quality of the crop yield (2), a number of experiments were performed in 1939 upon *N. rustica* grown in sand cultures. The plants were set out on May 16. From that date to July 3 the plants in all the crocks were

supplied with the same culture solution; and from July 3 to harvest (September 7), with various culture solutions, as indicated in table 4. Each plant was left with 10 leaves after topping. Immediately after being harvested, the tobacco leaves to be analyzed were conserved in ether fumes for 30 minutes and then dried in a desiccator at a temperature of 40 to 45° C. Samples for analysis were prepared from the blades of all the leaves from all four plants.[1]

### TABLE 3

*Effect of $NO_3^-$, $NO_2^-$, and $NH_4^+$ on the production of citric acid in the leaves of N. rustica*
(September 16, 1939)

| INFILTRATES | | CITRIC ACID IN FRESH LEAVES |
|---|---|---|
| | | *per cent* |
| NaNO₃ | 1st half of leaves.................................... | 0.815 |
| NaNO₂ | 2nd half of leaves.................................... | 0.688 |
| (NH₄)₂SO₄ | 1st half of leaves................................ | 0.661 |
| NaNO₂ | 2nd half of leaves................................ | 0.770 |
| NaNO₃ | 1st half of leaves................................ | 0.873 |
| (NH₄)₂SO₄ | 2nd half of leaves................................ | 0.737 |

### TABLE 4

*Effect of ammonia, nitrate, and nitrite nitrogen on the chemical composition of the leaves of N. rustica*

(1939 experiment—analyses on dry-weight basis)

| CULTURE SOLUTION | | | AVERAGE WEIGHT OF FRESH LEAF BLADES PER PLANT | CITRIC ACID | NICO-TINE | SUGAR | | NITROGEN | |
|---|---|---|---|---|---|---|---|---|---|
| Form of nitrogen | Concentration | | | | | Total | Reduc-ing | Protein | Non-protein |
| | N | K₂O | | | | | | | |
| | *mgm./l.* | *mgm./l.* | *gm.* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| NO₃.................... | 10 | 20 | 199.5 | 3.81 | 8.70 | 13.50 | 2.17 | 1.36 | 1.98 |
| NO₃.................... | 40 | 20 | 297.8 | 4.16 | 9.81 | 2.97 | 0.48 | 1.97 | 2.48 |
| NO₃.................... | 100 | 20 | 296.3 | 3.56 | 8.42 | 3.06 | 0.41 | 2.35 | 2.22 |
| NO₂.................... | 10 | 20 | 130.0 | 2.50 | 9.55 | 9.03 | 1.25 | 1.23 | 2.22 |
| NO₂.................... | 40 | 20 | 259.2 | 3.67 | 10.73 | 2.52 | 0.33 | 2.01 | 2.49 |
| NO₂.................... | 100 | 20 | 278.9 | 3.48 | 10.28 | 3.90 | 0.31 | 2.16 | 2.29 |
| NH₄.................... | 10 | 20 | 134.8 | 2.75 | 8.71 | 19.12 | 3.70 | 1.31 | 1.57 |
| NH₄.................... | 40 | 20 | 147.1 | 1.44 | 9.55 | 5.62 | 0.90 | 2.09 | 2.45 |
| NH₄.................... | 100 | 20 | 151.1 | 1.35 | 6.68 | 4.78 | 0.57 | 2.71 | 2.03 |

The results, given in table 4, confirm the conclusion that the leaves of *N. rustica* contain a greater quantity of citric acid when the plants are grown

[1] In the experiments conducted in the course of this investigation, citric acid was determined by extraction from sulfuric acid by the volumetric method, resulting in precipitation in the form of pentabromacetone (4); and malic acid was determined by precipitation from barium salts in alcohol (8).

in cultures containing nitrate nitrogen than when grown in cultures containing ammonia nitrogen. Nitrites, though intermediate in effect, approximate the nitrate more closely than the ammonium form.

The content of organic acids, especially citric acid, depends directly upon the carbohydrate and nitrogenous metabolism in plants, as is shown by the data on the sugar and nitrogen contents of the leaves of *N. rustica*.

Subsequent experiments, in 1940, were carried out to ascertain the effect of ammonia, nitrate, and nitrite nitrogen on the storage not only of citric acid but also of other acids, particularly malic acid. Again, the coarse variety of tobacco (*N. rustica*), which is the technical raw material for the production of malic acid as well as of nicotine and citric acid, was selected for study.

TABLE 5

*Effect of various concentrations of $NH_4^+$, $NO_2^-$, and $NO_3^-$ on the chemical composition of leaves of N. rustica*

(1940 experiment—analyses on dry-weight basis)

| CULTURE SOLUTION | | | AVERAGE WEIGHT OF FRESH LEAVES WITH BUDS PER PLANT | CITRIC ACID | MALIC ACID | SUGAR | | NICO-TINE | NITROGEN | |
|---|---|---|---|---|---|---|---|---|---|---|
| Form of nitrogen | Concentration | | | | | Total | Reducing | | Protein | Non-protein |
| | N | $K_2O$ | | | | | | | | |
| | *mgm./ l.* | *mgm./ l.* | *gm.* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| NH₄ | 10 | 20 | 211.5 | 3.60 | 7.01 | 4.12 | 2.92 | 11.68 | 1.36 | 2.47 |
| NH₄ | 40 | 20 | 373.9 | 1.75 | 4.11 | 0.85 | 0.31 | 12.98 | 1.80 | 4.32 |
| NH₄ | 100 | 20 | 412.1 | 1.13 | 2.21 | 0.48 | 0.22 | 8.14 | 2.08 | 6.58 |
| NO₂ | 10 | 20 | 214.5 | 4.54 | 5.93 | 5.75 | 3.20 | 10.22 | 1.60 | 2.47 |
| NO₂ | 40 | 20 | 342.6 | 3.67 | 6.27 | 6.96 | 0.73 | 10.71 | .... | 3.59 |
| NO₂ | 100 | 20 | 356.7 | 4.48 | 5.10 | 0.51 | 0.25 | 10.23 | 1.98 | 4.20 |
| NO₃ | 10 | 20 | 213.2 | 3.70 | 6.10 | 2.40 | 0.70 | 13.72 | 1.50 | 2.97 |
| NO₃ | 40 | 20 | 463.6 | 3.18 | 6.72 | 0.63 | 0.31 | 11.24 | 1.94 | 3.13 |
| NO₃ | 100 | 20 | 523.9 | 4.83 | 5.91 | 0.97 | 0.40 | 11.52 | 1.91 | 3.47 |

These experiments were likewise carried out in sand cultures with $(NH_4)_2SO_4$, $NaNO_2$, and $NaNO_3$ as sources of nitrogen. The seeds were planted in crocks on May 13. From the onset of germination until July 14, the plants in all the crocks were provided with the same culture solution, to which ammonium nitrate was added as the nitrogen source. Beginning with July 14, the culture solutions were varied according to the pattern given in table 5.

The crop was harvested on September 16, and samples for analysis were prepared as in the 1939 experiments. The data on crop yield and chemical composition of the leaves are presented in table 5.

The data presented in tables 4 and 5 warrant the following conclusions:

1. With nitrate nitrogen, the citric and malic acid contents are higher than with ammonia nitrogen. In its effect upon the storage of organic acids, nitrite nitrogen resembles more closely the nitrate form.

2. The malic acid content of *N. rustica* leaves is higher than the citric acid content.

3. Increasing the concentration of ammonia nitrogen from 10 to 100 mgm. brings about a decided reduction in the citric and malic acid contents, but no such reduction is observed when the concentrations of nitrate and nitrite nitrogen are increased.

4. Increasing the concentration of nitrogen, in both the ammonia and the nitrate form, brings about a marked reduction in the sugar content, with a simultaneous increase in the quantity of protein and soluble nitrogen. This indicates that the sugars are utilized in the synthesis of nitrogenous organic compounds in plants.

5. With ammonia nutrition the expenditure of sugars is connected with the synthesis of nitrogenous organic compounds, whereas under nitrate nutrition it is linked also with the formation of organic acids. In this regard it is noteworthy that the sugar content of tobacco leaves under nitrate nutrition is lower than in corresponding ammonia plants. Such diminution in the sugar content of leaves from nitrate plants indicates that nitrate nutrition requires an additional expenditure of sugar, due, on the one hand, to the reduction of nitrates in plants, and on the other, to the production of organic acids.

The difference between ammonia and nitrate nitrogen in regard to protein and carbohydrate metabolism and the metabolism of the organic acids found in plants can thus be established.

TABLE 6

*Changes in the composition of organic compounds in the leaves of N. rustica after 10 days' exposure to different forms of nitrogen*

(1940 experiment—analyses on dry-weight basis)

| CULTURE SOLUTION | | CITRIC ACID | MALIC ACID | SUGAR | | NITROGEN | |
|---|---|---|---|---|---|---|---|
| May 13–July 14 | July 14–24 | | | Total | Reducing | Protein | Non-protein |
| | | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| $NH_4NO_3$............... | $NH_4$ | 1.90 | 3.29 | 0.58 | 0.22 | 1.80 | 5.35 |
| $NH_4NO_3$............... | $NO_2$ | 3.35 | 5.89 | 0.73 | 0.34 | 1.73 | 4.39 |
| $NH_4NO_3$............... | $NO_3$ | 3.30 | 6.19 | 0.64 | 0.19 | .... | 3.42 |

The fact that a higher concentration of nitrate nitrogen leads to a certain reduction in organic acid content, as observed during these experiments, is perhaps best explained, not by the specific effect of nitrates, but by the fact that with an increase in the concentration of nitrogen the development of the plant is retarded, that is, a large concentration of nitrogen leads, as it were, to the rejuvenation of the plant. When all the plants grown on various concentrations of nitrogen are harvested on the same day, as in these experiments, they represent, from the biological standpoint, various ages.

To determine the specific effects of nitrate and ammonia nitrogen on the storage of citric and malic acids in plants of the same biological age, an experiment was performed with drip cultures. In this experiment the plants in all the crocks were provided, from May 13 to July 14, with the same culture solution, which contained $NH_4NO_3$ as the source of nitrogen, and from July 14 to July 24 with the various culture solutions. After the 10 days' exposure to the different solutions, the plants were harvested and the leaves analyzed for their content of citric and malic acids and other organic compounds. The results of this experiment are shown in table 6.

These data show that after 10 days of nitrate and nitrite nutrition the citric and malic acid contents of the tobacco leaves were markedly higher than after ammonia nutrition.

In view of the results obtained in all these experiments, the differences in the physiological effects of ammonia and nitrate forms of nitrogen on the metabolism of organic acids in plants may be regarded as definitely established. The fact that there is a relatively greater storage of organic acids under nitrate nutrition has likewise been noted by Vickery and others (11) in their latest investigations.

The established differences in the direction followed by biochemical processes in the plant organism, depending upon whether ammonia or nitrate nitrogen is available, throw new light on the possibility of controlling the composition of economically valuable organic products in the leaves of *N. rustica* by providing the plant with the requisite nitrogenous nutrition during vegetation. Before

TABLE 7

*Effect of various treatments with ammonia and nitrate nitrogen on the citric acid contents of tobacco leaves*

(1939 field experiment)

| FERTILIZER TREATMENT* | AVERAGE WEIGHT OF FRESH TISSUE PER PLOT | RATIO OF CITRIC ACID TO TOTAL DRY WEIGHT |
|---|---|---|
| | *kgm.* | |
| Control (no fertilizer) | 49.4 | 3.05 |
| Nc 75, P 60, K 90 | 52.0 | 3.23 |
| Nm 75, P 60, K 90 | 52.3 | 2.95 |
| Nc 112, P 60, K 90 | 58.3 | 3.26 |
| Nc 75, P 60, K 90, before planting, + Nc 37 at time of bud formation | 54.6 | 4.10 |
| Nm 112, P 60, K 90 | 59.4 | 3.88 |
| Nm 75, P 60, K 90, before planting, + Na 37 at time of bud formation | 64.2 | 2.75 |

* In kilograms per 50-sq.m. plot. Nc = Chilean nitrate, Nm = montan-saltpeter, Na = ammonium sulfate.

any such control can be effected, however, it is necessary to know what significance this difference in the effects of ammonia and nitrate nitrogen upon the storage of organic acids may have under field conditions if nitrogenous fertilizers in the form of salts of ammonia and nitrates are introduced.

With this end in view, a special field experiment was conducted in 1939 with various forms of nitrogenous fertilizers on the Staro-Yurevo State Tobacco Farm, Tambov region. The treatments and the harvest data are summarized in table 7.

The results of this experiment show that the treatment with montan-saltpeter and Chilean nitrate before transplanting did not cause any appreciable difference in the citric acid content of the *N. rustica*, for under these conditions of growth on montan-saltpeter, as a result of the comparatively rapid nitrification of ammonia nitrogen of the latter, the plants evidently fed in the main on nitrate nitrogen, as they did when grown on $NaNO_3$.

The inclusion of $(NH_4)_2SO_4$ and $NaNO_3$ in the nitrogen of the fertilizer (at the time of bud formation) brought about a drastic change in the citric acid content of the leaves: with $NaNO_3$, the citric acid content increased; with $(NH_4)_2SO_4$, it decreased. Consequently, on the basis of these laboratory and field experiments, it is safe to say that the differences in the metabolism of organic acids under ammonia and nitrate nutrition may be regarded as a fully established law.

Obviously, then, when various forms of nitrogenous fertilizers are used for the cultivation of tobacco, it is necessary to differentiate as to the use to which the plant is to be put. If the plant is to be used as raw material for the production of citric and malic acids, nitrate nitrogen serves the purpose better than does ammonia nitrogen. To avoid any reduction in the citric and malic acid contents of tobacco leaves, ammonia nitrogen should be omitted from the later fertilizer applications. In the early applications, before transplanting time, no particular difference between the ammonia and the nitrate forms will be evident, because of the conversion of ammonia into nitrates.

As has been pointed out, the results of the study of the metabolism of organic acids in plants as influenced by ammonia and nitrate nutrition have been the basis for the conclusion that nitrate nitrogen alters the oxidation-reduction processes in the plant by stimulating the oxidation processes, whereas the ammonia nitrogen stimulates the reduction processes. The stimulation of the oxidation or reduction processes has, however, been considered only from the standpoint of the storage of organic acids in the plants. It was assumed that the greater storage of organic acids in plants is conditioned by the relative predomination of oxidation processes. But this assumption might meet with objections. It may be held that the oxidation processes are stimulated not only by the oxidation of other organic substances in plants to organic acids, but also by the oxidation of the latter to carbonic acid, and as a result, in cases of intensified oxidation, the organic acid content of plants may first increase and then diminish.

To prove the interdependence between the storage of organic acids in plants and variations in the oxidation-reduction processes, the potential reducing capacity of the juice of *N. rustica* when supplied with ammonia and nitrate nitrogen was determined. The method, suggested in his time by Arenz (1), boils down to the quantitative determination in the juice of the plant of bivalent iron following the reaction of $FeCl_3$ with the juice. The results of these investigations, conducted in 1941, are presented in table 8.

The data show that far more bivalent iron was produced in the juice of the plant under ammonia nutrition than under nitrate nutrition. This indicates that when ammonia nitrogen is available, reduced organic compounds are stored in the plant to a much greater degree, because of the predominance of reducing processes, than is the case when plants are grown on nitrates.

Thus the determination of the potential reducing capacity of plant juice supports the conclusion drawn from the study of the metabolism of organic acids that nitrate nitrogen alters the oxidation-reduction processes in plants in the direction of an intensification of the oxidation processes, whereas ammonia

nitrogen alters them in the direction of an intensification of the reduction processes.

With this hypothesis as a basis, the assumption may be made that ammonia nitrogen will stimulate the storage in plants of reduced organic compounds such as caoutchouc, pyrethrine, and volatile oils, whereas nitrate nitrogen will retard the storage of such reduced products and will stimulate the storage of oxidized products, particularly of organic acids.

TABLE 8

*Effect of $NO_3$ and $NH_4$ ions as sources of nitrogen on variations in the potential reducing capacity of the juice of N. rustica leaves*

| NITROGEN SOURCES | $Fe^{++}$ PER 100 GM. OF DRY WEIGHT | | | | |
|---|---|---|---|---|---|
| | Sept. 11 | Sept. 17 | Sept. 20 | Sept. 26 | Oct. 7 |
| | *mgm.* | *mgm.* | *mgm.* | *mgm.* | *mgm.* |
| $NO_3^-$ | 60.80 | 93.61 | 97.71 | 91.92 | 65.70 |
| $NH_4^+$ | 81.25 | 111.67 | 115.66 | 165.15 | 140.12 |

TABLE 9

*Effect of ammonia, nitrate, and nitrite nitrogen on the yield of kok-saghyz*
(Vegetative experiment, 1940)

| CULTURE SOLUTION | WEIGHT OF 100 FRESH ROOTS | CAOUTCHOUC | YIELD OF CAOUT-CHOUC PER 100 ROOTS |
|---|---|---|---|
| | *gm.* | *per cent** | *gm.* |
| $NO_3^-$ + KCl ($\frac{1}{2}$ m.e.) | 775.0 | 2.85 | 5.69 |
| $NO_3^-$ + KCl (2 m.e.) | 880.0 | 3.05 | 6.58 |
| $NO_2^-$ + KCl ($\frac{1}{2}$ m.e.) | 727.0 | 2.95 | 5.74 |
| $NO_2^-$ + KCl (2 m.e.) | 811.0 | 3.10 | 6.91 |
| $NH_4^+$ + KCl ($\frac{1}{2}$ m.e.) | 1033.0 | 3.48 | 8.80 |
| $NH_4^+$ + KCl (2 m.e.) | 847.0 | 4.16 | 8.82 |

* Of dry tissue in 100 roots.

These propositions have been verified on a number of characteristic plants. The data on kok-saghyz, obtained in a sand culture experiment in 1940, may be cited as an example.

In this experiment, the plants in all the crocks were supplied with the same culture solution until August 10. On that date, after thorough washing first with tap water and then with distilled water, they were transferred to the laboratory system of culture solutions. The data obtained are given in table 9.

The results show that the percentage of caoutchouc and its actual yield per 100 roots of kok-saghyz are lower with nitrate and nitrite nutrition than with ammonia nutrition. Consequently, from the point of view of the content and yield of such reduced organic compounds as caoutchouc in kok-saghyz, ammonia nitrogen serves the purpose better than nitrate nitrogen.

## CONCLUSIONS

From experimental material cited in this paper on the effect of $NH_4^+$, $NO_2^-$, and $NO_3^-$ on the production of oxidized and reduced organic compounds in plants, the following conclusions may be drawn:

1. The general acidity and the content of citric and malic acids in the leaves of *N. rustica* increase when nitrate nitrogen is available and decrease when ammonia nitrogen is available. In this respect, nitrites, though occupying an intermediate position, are more like the nitrates.

2. The general acidity and the content of citric and malic acids in the leaves of *N. rustica* fall with an increase in the concentration of ammonia nitrogen and rise with an increased concentration, up to a definite limit, of nitrate nitrogen.

3. Changes in the content of organic acids in plants under ammonia or nitrate nutrition indicate that nitrate nitrogen, being the oxidized form, gives rise in the plant organism to conditions stimulating the oxidation processes, whereas ammonia nitrogen, the reduced form, gives rise to conditions stimulating the reduction processes.

The organic acid contents of plants under ammonia or nitrate nutrition are inversely related to the potential of the reducing capacity of the plant juice, *i.e.*, the lower the organic acid content, the higher is the reducing capacity of the plant, and *vice versa*.

4. In contradistinction to ammonia, nitrogen in the form of nitrates gives rise to definite features in the metabolism of carbohydrates in the plant: the loss of sugars under ammonia nutrition is linked, in the main, with the synthesis of nitrogenous organic compounds; under nitrate nutrition the loss of sugars is linked not only with the synthesis of nitrogenous compounds but also with the more intensified production of organic acids.

5. Intensifying the reduction processes in the plant organism, ammonia, in contradistinction to nitrate and nitrite nitrogen, stimulates the greater storage of caoutchouc in the roots of kok-saghyz.

6. Under nitrate nutrition not only do the citric and malic acid contents of plants increase, but there is likewise an increase in other valuable organic acids, particularly ascorbic acid (vitamin C). Under ammonia nutrition, on the other hand, there is an increase not only in the caoutchouc content of kok-saghyz, but also in other reduced products such as pyrethrine in the Dalmatian daisy and volatile oils in essential oil plants.

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# SPRAY RESIDUES AND CROP ASSIMILATION OF ARSENIC AND LEAD[1]

J. S. JONES AND MILES B. HATCH[2]

*Oregon Agricultural Experiment Station*

From the experimental data of an earlier paper (7) and the recorded observations of other investigators it is plain that in the depth of soil stirred by the implements commonly used in commercial orchard cultivation. a major soil problem develops with the aging of the trees. Inevitably, as commercial orchards approach maturity there will have accumulated in their surface soil zones to a depth of 6 to 8 inches, excessively large amounts of potentially harmful inorganic spray residue compounds—chiefly those of arsenic and lead.

Indicative of the complexity of soil and crop problems that are traceable to this situation are the experiences and observations of Morris (12), Snyder (15), and Blodgett (2). The first-mentioned points out the coincidence of failures in cover crop growth with attainment of maturity in the development of the trees in well-cared-for commercial orchards and also the frequency of early decline in the productiveness of individual trees. Snyder recounts his observations on the difficulties, discouragements, and even complete failures in production encountered by those who succeeded the orchardists in the use of orchard lands and attempted the growth of the more shallow-rooted food and forage crops for human and livestock consumption. Blodgett gives evidence that injury to young peach and apricot trees grown on old apple orchard land is traceable to the accumulation of arsenic residues in the soil. From these and similar observations by others in various orchard sections of the Pacific Northwest, it is evident that coincident with the growth of commercial orchards soil conditions develop that not only shorten the life of the trees but make difficult the profitable use of reclaimed orchard lands in the growth of such food and forage crops as normally follow the orchards in rotation. On occasion it has been intimated, too, that in addition to lessened yields may come impaired nutritional value of both food and forage crops through increased assimilation of both arsenic and lead. The principal objective of this paper is the presentation of some analytical data bearing directly on this last-mentioned point.

REVIEW OF LITERATURE

That increase in absorption and assimilation by farm crops of the essential inorganic elements follows the enrichment of soils with compounds containing those elements appears to be definitely established by experiment and observation. Typical of many that might be cited is the experience of Reimer and Tartar (13), who noted an increase of approximately 50 per cent in the sulfur content of alfalfa when grown with sulfur fertilization in contrast to that grown without such fertilization in soils that are notably low in the sulfur content. Likewise through an experimental period of several years, first Lewis and Powers (9), working with iodine, and later Powers and graduate students,[3] working with boron, manganese, and zinc, noted substantial increases in crop absorption and utilization of that group of the so-called minor elements following soil treatment with inorganic compounds containing them. In contrast, however, and of particular interest in this connection because the element in question is classed as both nonessential and harmful to plant growth is the pointed observation by Williams (16) on selenium. It is to the effect that although that element is assimilated to their detriment by many species of plants, the total amount is not in proportion to the selenium content of the soils in which they grow.

It is commonly believed that arsenic and lead each functions adversely to the welfare of both plant and animal bodies into which it may be carried along with nutrient elements in normal processes of growth. The evidence against lead, however, is not so clear-cut as that against arsenic. Hammett (6) determined for lead a peculiarly harmful combination with certain protein units of cell protoplasm in onion, bean, and corn roots. Keaton (8), in contrast, found that certain lead compounds stimulated growth of barley. Auchter (1) and Mc-Murtrey and Robinson (11) have suggested the probability of physiological disturbances of greater or less import following consumption by livestock of forage plants containing abnormal amounts of either element. Moreover, as earlier literature records, each of these elements has figured prominently in alleged livestock poisoning by pasture grasses and other forage that had grown in soils over which smelter fumes containing arsenic had drifted or through which drainage waters from lead smelter tailings had percolated. The literature is replete with reminders that feeders of livestock in particular view with genuine alarm any set of circumstances that tends to increase the arsenic and lead content of livestock feeds. It would seem reasonable to be concerned under similar circumstances also with the effect of each on the welfare of human beings.

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In this investigation inquiry centers on the increased readiness with which each element is assimilated by food and forage crops from soils that have been substantially enriched in their arsenic and lead content by some 20–25 years of spray residue accumulations. Utilization of such crops for food and feeding purposes will constitute, for years to come, an important channel along which these elements will pass for whatever measure of harm they may do the animal body.

<div align="center">EXPERIMENTAL</div>

*Selection, planting, and care of the experimental plats*

Following a period (1936–1937) of greenhouse experimentation in growing certain forage crops in commercial orchard soils that were more or less highly saturated with spray residue compounds, soil plats in the open fields were decided upon as being more convenient and more practical than potted soils in this work for the experimental growing of food and forage crops. In soil plats, it was reasoned, there would be the same degree of freedom that will prevail eventually in the open fields for roots to penetrate soil depths below the zone of greatest spray residue accumulation and, therefore, a closer imitation of future open field conditions in growing the same crops. Obviously, the plats required for this kind of experimentation would have to be located outside the boundaries of any commercial orchard and still be representative of some soil series and types that are commonly used for commercial orchard purposes. That objective was gained in the set-up described in the following:

In each of four leading commercial orchard sections of the state a site was chosen in the open, on soil of identical series and type with that of a nearby mature commercial orchard. Each was sufficiently large for two plats approximately 10 by 15 feet. The surface soil of the area that was to become plat 1 was loosened to a depth of approximately 8 inches, dug up, and discarded. In its place was substituted surface soil from a nearby commercial orchard to the same depth. The soil of the area that was to become plat 2 was left undisturbed and was, therefore, in its native condition with respect to arsenic- and lead-containing minerals. In these pairs of plats such food and forage crops as are characteristic of each of the four commercial orchard sections were grown experimentally as they would be under otherwise normal above-ground conditions. The objective was the accumulation of several years' cropping experience and laboratory analytical data bearing directly upon the degree to which the crops chosen for experimentation might increase their assimilation of arsenic and lead over the normal for that soil when their root systems occupied, mainly or in part, soil zones that were substantially charged with inorganic spray residue compounds—the accumulated waste of 20 to 25 years of commercial orchard spraying operations. In like manner will food, forage, and grain crops be grown in these soils for household and livestock consumption when commercial orchards have rounded out a normal lifetime and given way in rotation to them.

In table 1 the arsenic and lead content of each of the four sets of soils is shown. The analytical data on arsenic- and lead-containing minerals for each of the soils in its native condition were obtained on a mixture composited from five samples—one taken from near each corner and one from the center of each plat. The corresponding data for each of the orchard soils are averages of analytical data on each of five individual samples from each plat—one from near each corner and one from the center. The analytical data reveal remarkable uniformity in the distribution of the spray residue compounds in these soils. The Hood silt and Neal silty clay loam are lighter in texture than either of the other two. In their normal condition, all plats contain more lead than arsenic— three of them, substantially more. Twenty to twenty-five years of spraying operations have increased the arsenic of the four soils from 20 to 30 times their original content of that element and their normal content of lead from 13 to 40 times. Though the presence of native minerals containing arsenic and lead

## TABLE 1

*Arsenic and lead content of soils used in experimental soil plats*

In     parts     per     million—air-dry     basis

|  | CENTRAL STATION CORVALLIS MELBOURNE CLAY LOAM | | HOOD RIVER STATION, HOOD RIVER HOOD SILT | | MEDFORD STATION, MEDFORD MEYER CLAY ADOBE | | SOUTHERN OREGON STATION, TALENT NEAL SILTY CLAY LOAM | |
|---|---|---|---|---|---|---|---|---|
|  | AS₂O₃ | PbO | AS₂O₃ | PbO | AS₂O₃ | PbO | AS₂O₃ | PbO |
| Soils in native condition (composite of five samples) | 4.0 | 17.7 | 2.7 | 3.2 | 6.1 | 16.5 | 5.3 | 21.3 |
| Soils from commercial orchards (average of analytical data on each of five samples) | 87.5 | 236.7 | 53.0 | 127.4 | 126.3 | 351.0 | 152.0 | 405.0 |
| Times greater in sprayed soils | 21.1 | 13.4 | 19.6 | 39.8 | 20.7 | 21.3 | 28.7 | 19.0 |

enabled growing crops in the check plats at each station to absorb and assimilate both elements, it is plain that in the plats of accumulated spray residue content each element was more abundant and in more readily available form. In the latter, there could be maximum absorption of each element by the several crops grown experimentally.

The first year's cropping experience, in 1937, suggested some obviously necessary changes in cropping procedure. In particular it emphasized the necessity for selecting the more adaptable of both food and forage crops for the remaining period of experimental work. The shallow-rooted crops, those whose root systems are not sufficiently extensive to enable penetration to the soil zone below that of greatest spray residue accumulation, did not lend themselves satisfactorily to this series of experiments. For the most part they were discontinued after the first year's attempt to grow them. The number of crops, then, was narrowed to include only the hardier ones and those apparently least

sensitive to the presence of spray residue elements. Cultivation was by hand and limited in amount. Irrigation was employed at the Hood River station and at the Medford and Talent stations. Normal rainfall sufficed for the crops on the plats of the Central station at Corvallis.

### Harvesting and selection of laboratory samples

With few exceptions, the several crops were harvested as they would be normally in each of the four experimental areas for whatever use might be intended. Selections were made of whole plants. When these were gathered, the roots were flushed liberally in running water to free them of soil particles. These "samples" were then packaged and sent to the chemical laboratory of the Central Experiment Station at Corvallis. Here the several parts, roots, stalks, leaves, and edible portions, were thoroughly washed with a scrubbing brush in running water. They were then cut into convenient pieces and dried in vacuum drying ovens. Finally the dried plant parts were ground in preparation for chemical analysis. All analytical data are expressed in parts per million of dry plant parts.

### Analytical methods

Previous experience in similar work guided the choice of analytical methods for arsenic and lead in both soil and crop samples.

*Arsenic.* Arsenic in both soil and plant material was determined by the method of Allcroft and Green.[4] It consists essentially of the wet combustion of 2.50 gm. of soil or of 5 to 20 gm. of dried plant material with the customary mixture of nitric and sulfuric acids. Activated shot zinc and stannous chloride are added to the digest and the resultant arsine bubbled into silver nitrate solution. The arsenic is then titrated with 0.002 $N$ iodine solution. This method was found to be more satisfactory than either the Gutzeit or the bromate-distillation method used in the work previously reported (7). The analytical data in table 2 show that large amounts of plant material containing very small amounts of arsenic can be manipulated in a highly satisfactory manner. As a guard against error from extraneous sources in the arsenic analyses a "blank" determination was made with each set of unknowns. Recovery of arsenic added to plant material averaged 95 per cent.

*Lead.* The A.O.A.C. method for lead in food as outlined in the fifth edition of "Official Methods" was used for the determination of lead in both soil and plant material. Soil samples weighing 2.50 gm. were first ashed in platinum dishes for 2 hours at 450° C.; plant materials weighing 20 gm. likewise were ashed in platinum at the same temperature for 15 to 16 hours. In either case the residue was extracted with HCl and the lead recovered from the leached solution with dithizone. Electrolysis of the lead followed by titration of the lead peroxide with 0.0025 $N$ sodium thiosulfate completed the analysis. Recovery of lead added to plant material averaged 96 per cent. As in the arsenic analyses, a "blank" determination was made with each set of unknowns.

[4] *Biochem. Jour.* 29: 824–833 (1935).

*Presentation of analytical data*

The analytical data for each of the crops grown on the four stations for each of the three years of experimentation were compiled independently and studied for any suggestion of change in the cropping procedure. No fundamental change from that originally planned was found to be advisable. The first year's experience taught, however, the futility of trying to grow any but the more adaptable of the food crops in the plats of high spray residue content. Obviously it was of no avail to grow in a check plat any crop that would not make at least fair growth in the adjacent plat of spray residue content. The relative assimilation of the two elements, arsenic and lead, under both normal and abnormal conditions of growth imposed by reason of substantial accumulations of

TABLE 2

*Duplicate arsenic determinations on plant material*

| DESCRIPTION | SAMPLE | AS$_2$O$_3$ | |
|---|---|---|---|
| | gm. | mgm. | p.p.m. |
| Kale, leaves—unsprayed soil........... } | 15.0 | .248 | 16.50 |
| | 5.0 | .092 | 18.50 |
| Alfalfa, leaves and stems—sprayed soil. } | 12.0 | .240 | 20.00 |
| | 12.0 | .239 | 19.99 |
| Bean, vines—sprayed soil.............. } | 20.0 | .124 | 6.20 |
| | 20.0 | .126 | 6.30 |
| Beet, tops—sprayed soil.............. } | 10.0 | .078 | 7.80 |
| | 10.0 | .069 | 6.90 |
| Pea, vines—unsprayed soil............ } | 20.0 | .006 | 0.30 |
| | 20.0 | .005 | 0.25 |

the spray residue compounds of those elements was being studied. The analytical data on as many of the crops as seemed to have matured normally were assembled yearly by stations and summarized on completion of the third year's work. Typical analyses from the 3 years' summary of analytical data are shown in table 3. Not all the crops, even of those least susceptible to spray residue influence on growth, succeeded simultaneously on all of the four series of plats. This renders impracticable any attempt to evaluate here the influence of soil texture on crop absorption and assimilation of the spray residue elements. It will be recalled that the Hood silt and Neal silty clay loam are lighter than the other two of the four soils.

To make practicable the use of all the analytical data summarized at the end of the 3-year period of experimentation, tables 4, 5, and 6 were planned.

In table 4 averages of all analytical data are shown solely on the basis of above-ground and below-ground parts and roots. Tops, stalks, and leaves are parts that normally will figure in the feeding of livestock. By "edible portions"

TABLE 3

*Typical analyses of plant parts*

From summarized analytical data, in p.p.m.-dry basis

| CROP AND PART | CHECK PLATS | | COMMERCIAL ORCHARD SOIL PLATS | |
|---|---|---|---|---|
| | $AS_2O_3$ | PbO | $AS_2O_3$ | PbO |
| *Central Station* | | | | |
| Bean | | | | |
|     Vines.......................... | 0.24 | 1.85 | 2.40 | 4.31 |
|     Roots.......................... | 0.38 | 1.79 | 7.64 | 8.27 |
| Carrot | | | | |
|     Tops........................... | 0.00 | 2.61 | 0.75 | 4.72 |
|     Root, edible................... | 0.42 | 0.48 | 0.24 | 2.66 |
| Pea | | | | |
|     Vines.......................... | 0.39 | 1.70 | 2.69 | 7.32 |
|     Edible (green seed)............. | 0.08 | 0.15 | 0.13 | 0.29 |
|     Roots.......................... | .... | 8.92 | .... | 24.73 |
| Vetch | | | | |
|     Hay............................ | 1.61 | 3.80 | 2.54 | 5.08 |
|     Roots.......................... | 9.44 | 3.87 | 20.90 | 24.67 |
| *Hood River Station* | | | | |
| Egg plant | | | | |
| Edible (peeled).................. | 8.11 | 19.14 | 26.00 | 35.00 |
|     Roots.......................... | 1.30 | 5.00 | 13.00 | 7.37 |
| Onion | | | | |
|     Tops........................... | 4.22 | 10.28 | 11.69 | 10.28 |
|     Edible (bulb).................. | 0.47 | 1.05 | 0.47 | 3.77 |
| Pea | | | | |
|     Vines.......................... | 2.38 | 8.13 | 6.68 | 9.15 |
|     Edible (green seed)............. | 0.53 | 0.84 | 0.64 | 2.07 |
| Pepper | | | | |
|     Edible......................... | 0.52 | 0.91 | 0.62 | 1.79 |
|     Roots.......................... | 2.08 | 8.71 | 9.10 | 13.04 |
| *Medford Station* | | | | |
| Clover, white, pasture............. | 4.81 | 6.17 | 8.24 | 13.72 |
| Corn, stalks...................... | 0.94 | 7.51 | 3.64 | 12.44 |
| Pea | | | | |
|     Vines.......................... | 3.73 | 6.59 | 7.53 | 9.89 |
|     Edible (green seed)............. | 0.05 | 0.42 | 0.05 | 0.42 |
|     Roots.......................... | 1.58 | .... | 30.00 | .... |
| Tomato | | | | |
|     Vine........................... | 8.92 | 6.30 | 15.16 | 13.61 |
|     Roots.......................... | 0.34 | .... | 2.55 | 32.10 |
| *Southern Oregon Station* | | | | |
| Alfalfa | | | | |
|     Hay............................ | 2.60 | 5.32 | 4.45 | 9.21 |
|     Roots.......................... | 1.03 | 2.75 | 4.14 | 7.75 |
| Beet | | | | |
|     Tops........................... | 1.93 | 4.46 | 4.60 | 8.23 |
|     Root, edible................... | 0.45 | 0.68 | 1.70 | 1.91 |
|     Roots.......................... | 1.67 | .... | 26.70 | .... |

TABLE 3—*Continued*

| CROP AND PART | CHECK PLATS | | COMMERCIAL ORCHARD SOIL PLATS | |
|---|---|---|---|---|
| | AS₂O₂ | PbO | AS₂O₂ | PbO |
| Kale | | | | |
|   Leaves........................... | 0.36 | 1.65 | 1.30 | 1.95 |
|   Roots............................ | 0.52 | 3.00 | 23.10 | 8.62 |
| Lettuce | | | | |
|   Edible (leaves).................. | 0.16 | 3.60 | 0.42 | 4.59 |
|   Roots........................... | 0.62 | 1.64 | 14.50 | 22.36 |
| Tomato | | | | |
|   Edible (fruit).................. | 0.11 | 1.19 | 0.13 | 1.19 |
|   Roots.......................... | 0.65 | 5.22 | 16.95 | 8.70 |

TABLE 4

*Summary of all analytical data**

In parts per million—dry basis

| DESCRIPTION | CENTRAL STATION | | HOOD RIVER BRANCH STATION | | MEDFORD BRANCH STATION | | SOUTHERN OREGON BRANCH STATION | |
|---|---|---|---|---|---|---|---|---|
| | AS₂O₂ | PbO | AS₂O₂ | PbO | AS₂O₂ | PbO | AS₂O₂ | PbO |
| Tops (leaves and stems)—unsprayed soil...................... | 0.71 | 1.60 | 7.54 | 19.54 | 6.32 | 17.27 | 2.08 | 5.88 |
| Tops (leaves and stems)—sprayed soil........................ | 2.13 | 4.55 | 9.69 | 21.76 | 8.73 | 22.37 | 3.64 | 7.53 |
|   Times greater in sprayed soils... | 3.0 | 2.8 | 1.3 | 1.1 | 1.4 | 1.3 | 1.8 | 1.3 |
| Edible portion—unsprayed soil..... | 0.13 | 0.08 | 0.65 | 0.72 | 1.07 | 2.00 | 0.33 | 0.62 |
| Edible portion—sprayed soil....... | 0.15 | 0.72 | 0.76 | 2.00 | 3.95 | 2.35 | 1.53 | 1.09 |
|   Times greater in sprayed soils... | 1.2 | 9.0 | 1.2 | 2.7 | 3.7 | 1.2 | 4.6 | 1.7 |
| Roots—unsprayed soil............. | 2.08 | 3.46 | 1.00 | 5.46 | 1.78 | 1.74 | 1.02 | 3.48 |
| Roots—sprayed soil.............. | 9.85 | 18.76 | 3.93 | 11.11 | 10.51 | 14.68 | 15.77 | 9.33 |
|   Times greater in sprayed soils... | 4.7 | 5.4 | 3.9 | 2.0 | 5.9 | 8.4 | 15.4 | 2.7 |

* A total of 166 analyses for arsenic and 147 analyses for lead on plant parts from check plats and the same numbers of analyses for arsenic and lead on corresponding plant parts from the spray-residue-containing plats.

is meant here those portions of food crops that normally are consumed in the household. Roots are the below-ground portions of the plants, including the physiological organs of absorption. They generally would be inaccessible to livestock, excepting such as normally graze very closely or freely root in search of succulent plant parts. In the averages some 8 to 10 different crops at each of the stations for each of the three years are involved. For reasons previously indicated, however, they are not identical throughout. In the analytical data of tables 1 and 4 would seem to be a reasonable and logical basis for answers to questions bearing upon the relationship between soil accumulation of spray residue elements and the response of food and forage crops in increased absorp-

tion and assimilation of those elements. It will be noted that with increases in the arsenic content of the soil, ranging from 20 to 30 times the original content, corresponding increases in crop absorption ranged from 1.3 to 3.0 times in aboveground parts (leaves and stems) and from 4 to 15 times in the roots. With increases in the lead content of the soil, through spray residue accumulation of that element, ranging from 13 to 40 times the native content, corresponding

TABLE 5

*Average (all plats) arsenic and lead content of each portion of all plants analyzed*

In parts per million—dry basis

| DESCRIPTION | AS$_2$O$_3$ | PbO |
|---|---|---|
| Tops (leaves and stems)–unsprayed soil........... | 4.71 | 12.14 |
| Tops (leaves and stems)—sprayed soil............. | 6.66 | 15.08 |
| Times greater in sprayed soils.................. | 1.4 | 1.2 |
| | | |
| Edible portion—unsprayed soil.................... | 0.60 | 0.86 |
| Edible portion—sprayed soil..................... | 1.58 | 1.38 |
| Times greater in sprayed soils.................. | 2.6 | 1.6 |
| | | |
| Roots—unsprayed soil............................ | 1.39 | 3.99 |
| Roots—sprayed soil.............................. | 9.34 | 12.28 |
| Times greater in sprayed soils.................. | 6.7 | 3.1 |

TABLE 6

*Average arsenic and lead content of the entire plant*

Average of all analytical data, in parts per million—dry basis—for all plants grown on unsprayed and sprayed soil

| DESCRIPTION | AS$_2$O$_3$ | PbO |
|---|---|---|
| Plants grown on unsprayed soil.................... | 2.77 [166]* | 7.26 [147] |
| Plants grown on sprayed soil..................... | 6.31 [166] | 11.19 [147] |
| Times greater in sprayed soils.................. | 2.3 | 1.5 |

* Figures in brackets indicate total number of samples involved.

increases in lead assimilation by the same crops ranged from 1 to 3 times in aboveground parts and 2 to 8 times in their roots. Noticeable is the fact that edible portions of the crops assimilated the smallest amounts of both arsenic and lead. The amounts, too, are in substantial agreement with amounts found by Fleming *et al.* (4) and by McLean *et al.* (10) in a series of investigations having a somewhat similar objective.

In table 5 all analytical data are assembled as they would be if of common origin. Table 6 is the final summary of all analytical data.

## DISCUSSION

It is reasonably well established that arsenic and lead are normal components of agricultural soils and likewise of food, forage, and other crops, although neither element functions definitely in plant growth. Until recently these facts aroused little or no concern on the part of the consuming public or in the minds of those who have in charge the feeding of livestock. That situation is changing with more common realization of the fact that as commercial orchards attain maturity and give way in rotation with field crops their surface soil zone accumulations of the more readily soluble compounds of arsenic and lead may have the effect of increasing substantially the arsenic and lead content of relatively large acreages of such crops as are commonly grown for food and forage. It is logical to anticipate some increase, and with that possibility there is naturally some concern on the part of those whose responsibility it is to ration either human beings or livestock.

The work reported here was undertaken to determine experimentally what is reasonably to be expected of food and forage crops in the way of increased absorption and assimilation of arsenic and lead under the fairly well defined abnormal soil conditions that must prevail when such crops succeed commercial orchards in rotation. Under the same conditions and in much the same way as they were grown experimentally in the course of this work will the same and similar crops be grown in one state alone on some 50,000 acres of what normally should be the most productive of soils, when presently commercial orchards give way in rotation to them. That acreage must be multiplied many times if a national viewpoint is substituted for one limited by state boundaries.

The first two of the four soils used experimentally have a spray-receiving history of approximately 22 years. For the other two that period is longer by some six or eight years. It is apparent that in each case the annual increase over the soil's original content of arsenic and lead has been substantial and obviously each element is in more readily available combination for assimilation by growing crops than is the case when native soil minerals alone constitute the source of those elements. From the failure generally of shallow-rooted crops planted in the earlier part of this experimental period and more recent observations of larger scale plantings of such crops under similar conditions, it is reasonable to conclude that in general the early and more shallow-rooted of the vegetable crops will prove to be unprofitable in the early stages of the redevelopment of commercial orchard lands. In crops that are sufficiently deep-rooted to overcome the initial discouraging conditions for growth in commercial orchard soils in process of reclamation, consumers and those who will have in charge the feeding of livestock must reckon with some increases over the normal assimilation of both arsenic and lead regardless of soil type. Fortunately the significances of these increases can be evaluated now with a fair degree of accuracy and understanding both in the light of legally established tolerances for these elements in foodstuffs and in the light of recorded feeding experiments. It will be recalled that the legal tolerance for arsenic on fruit and vegetables is 3.6 p.p.m. $As_2O_3$, and here it will be noticed that the edible parts of the plants grown in sprayed-

over soils in this series of experiments containing on the average $\frac{1}{14}$ of this amount of $As_2O_3$ when calculated on the fresh basis. Livestock in feeding on leaves and stems of plants grown in these sprayed-over soils would have to consume daily in the hundreds of pounds of fresh material to obtain enough arsenic to approximate in intake the minimum lethal dose of inorganic arsenic as determined by Green and Dijkman (5). Moreover, investigations by Fairhall and Miller (3) involving the feeding of rats and by Seddon and Ramsay (14) in feeding sheep indicate that compounds of lead in comparable amounts are less toxic than those of arsenic. One is bound, then, to note that mechanically adhering dust and dirt might easily prove to be the more dangerous source of either or both elements particularly in the feeding of livestock.

### SUMMARY

A review of the literature leads to the conclusion that soil fertilization with compounds of chemical elements that function definitely in crop growth results in substantial increases in crop assimilation of those elements. Just as positive is the evidence of increased assimilation of those same chemical elements by animal bodies whose food or feedstuffs are traceable to soils of high natural fertility or to soils that have been substantially enriched by consistent fertilizer practice. The evidence of published literature points far less clearly to definite conclusions when in turn it is concerned with other chemical elements that likewise are of common occurrence in plant parts but perform no specific function in either plant or animal growth. Prominent in this group are the elements considered in this paper—arsenic and lead.

On occasion each element has figured prominently in the poisoning of both human beings and livestock when conveyed mechanically to the victim by adherence of its compounds to food or feedstuffs. For this reason perhaps there is frequently expressed concern over situations created by the return of commercial orchard lands, following maturity of the trees and declining yields, to the production of annual food and forage crops. Some suspicion prevails that such crops might acquire through normal processes of growth sufficiently large quantities of arsenic and lead as to become a source of danger to the welfare of human beings and livestock should they become the sole source of animal food and nourishment. The several years of field and laboratory work summarized here would seem to be a fair test of that possibility. It clearly supports a negative conclusion. Instead, the experience gained and observations made in the conduct of these experiments give warning that inability on the part of many of the more shallow-rooted crops to make even fair growth and reduced yields on the part of others will be the most discouraging of the several factors involved in the reclamation of commercial orchard lands for food and forage crop production.

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# EFFECT OF TYPE OF SOIL COLLOID ON CATION-ADSORPTION CAPACITY AND ON EXCHANGEABLE HYDROGEN AND CALCIUM AS MEASURED BY DIFFERENT METHODS[1]

ADOLF MEHLICH

*North Carolina Agricultural Experiment Station*

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Since it was discovered that the titration curves of H-clays resemble those of weak acids, numerous methods have been proposed for measuring the cation-adsorption capacity and exchangeable H of soils. The values obtained differed markedly depending on the method used. To eliminate the empirical features introduced by the particular method used, Bradfield and Allison (8) in 1933 defined a saturated soil as "one which has reached equilibrium with a surplus of $CaCO_3$ at the partial pressure of $CO_2$ existing in the atmosphere and at a temperature of 25° C." By means of the method described, the saturation deficit or exchangeable hydrogen on natural soils is measured. For the direct determination of the cation-adsorption capacity by this method, H-soils must first be prepared. As far as the writer knows, no systematic study has been made in which the equilibration method is compared with other methods. Because of the significance of exchange properties in relation to soil development, nutrient conservation, plant nutrition, and liming, it is desirable that the values obtained by different methods be related to a single standard.

Therefore, an investigation was undertaken in which materials representing the organic, the hydrous mica, the 2:1 and the 1:1 lattice type of soil colloids were used. The following studies were made: (*a*) comparison of the $CO_2$ equilibration and ammonium hydroxide volatilization methods for the determination of the saturation point; (*b*) comparison of the $CO_2$ equilibration, the ammonium hydroxide, the ammonium acetate, the barium acetate, and the barium chloride-triethanolamine methods for determining the cation-adsorption capacity and exchangeable H; (*d*) comparison of the relative efficiency of ammonium and barium ions in replacing exchangeable calcium in the presence and absence of calcium carbonate.

## MATERIALS AND METHODS

### Source and preparation of soils and minerals

The 2:1 lattice type of colloids used were bentonite (Volclay), Putnam, and White Store. Volclay bentonite is a commercial product. The Putnam colloid was obtained from Dr. C. E. Marshall, of the Missouri Agricultural Experiment Station. The White Store was from the $B_2$ horizon and is the same as that used in a previous study (19).

Representatives of the 1:1 lattice type used were "Kamec" kaolin, halloysite, and subsoil samples of Cecil and Durham. "Kamec" kaolin is a commercial product. Halloysite was obtained from Dr. S. B. Hendricks, of the Bureau of Plant Industry. The Durham was obtained from the $B_1$ horizon of a soil near Raleigh, North Carolina. Its properties are described in a previous paper (19). The Cecil came from the $B_1$ horizon of a soil in Wake County, North Carolina. Its titration curve is shown elsewhere (16).

The mica-like colloids were illite, obtained from Dr. S. B. Hendricks, and a Collington subsoil (greensand) from the Camden area of New Jersey.

The organic systems were represented by peat, Portsmouth A, and Portsmouth B. The peat came from the Florida Everglades Substation. The Portsmouth A was a surface sample from Craven County and the Portsmouth B a surface sample from the vicinity of Chadbourn, North Carolina. They contained 6.2 and 6.8 per cent organic matter, respectively, the inorganic fraction being largely quartz sand.

Colloid separates were used from Durham, Cecil, Collington, Putnam, and illite. The other materials and soils were used without separation.

Hydrogen-soils were prepared by leaching with two symmetry concentrations of HCl. This treatment did not completely remove the metal cations, but it reduced inaccuracies in the titration values arising from the presence of Al. The exchangeable cations were determined and included in the calculations of the adsorption capacity when determined by the $CO_2$ equilibration and the $NH_4OH$ methods.

Soils of various degrees of saturation with calcium were prepared by treating the H-soils with appropriate amounts of $Ca(OH)_2$, aspirating with air, filtering, air-drying, and grinding to pass a 40-mesh sieve. The soluble calcium removed in the filtrate was determined quantitatively by the method of Chapman (10)). In samples receiving an excess of $Ca(OH)_2$, the residual $CaCO_3$ was determined by the method of Schollenberger (29), except that a Knorr type alkalimeter was used.

### Analytical methods

*Equilibration procedure.* The method of Bradfield and Allison (8), including minor modifications by Naftel (22), was used.

*Ammonium hydroxide procedure.* The method followed was essentially that of Keenen and O'Leary.[2] Amounts of soil or colloid giving between 0.5 and 1.5 m.e. of exchangeable cations were weighed into 25-ml. beakers, and 5 ml. of 0.05 to 1.0 $N$ $NH_4OH$ was added. The suspensions were then thoroughly stirred, covered, and allowed to stand overnight. The excess $NH_3$ was allowed to escape, and the samples were evaporated to dryness in a forced-draft oven at 40° C. The samples were then transferred into Kjeldahl flasks, and the $NH_3$ was distilled with MgO into 30 ml. of 2 per cent boric acid and titrated with standard

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[2] Private communication. The method and some experimental data obtained were made available through the courtesy of Dr. F. G. Keenen of the Chemical Division, Du Pont Laboratories, Wilmington, Delaware.

acid, bromocresol green being used as an indicator. With the organic soils a phosphate buffer (30) was substituted for MgO.

*Ammonium acetate procedure.* Amounts of soil giving between 0.25 and 0.5 m.e. of exchangeable cations were weighed into crucible holders fitted with small, moistened filter paper discs. Fifty ml. of $N$ or 0.1 $N$ $NH_4OAc$ at pH 7.0 was then leached through the soils, and the excess $NH_4OAc$ was removed by washing with ethanol. The $NH_4$ thus held was determined by distillation with MgO into boric acid and titration with standard acid.

The exchangeable H was determined in the leacheate by back-titrating to pH 7 with 0.05 $N$ $NH_4OH$ using a glass electrode. The exchangeable Ca was determined by the method of Chapman (10). Organic matter, whenever present, was removed with 10 per cent $H_2O_2$. For titrating the oxalic acid, 0.025 $N$ $KMnO_4$ was used.

*Barium acetate procedure.* The amounts of soil or colloid used in this and in the barium chloride-triethanolamine procedure were in all cases twice as large as those used in the $NH_4OAc$ method. The samples were leached with 50 ml. of 0.2 $N$ $BaOAc$, washed with 50 ml. of $H_2O$, and the leachate made up to a volume of 100 ml. The exchangeable H was determined in a 25-ml. aliquot by back-titrating with 0.05 $N$ $Ba(OH)_2$, using phenolphthalein as the indicator. The exchangeable Ca was determined as follows: To a 25-ml. aliquot, 25 ml. of 0.1 $N$ $H_2SO_4$ and 1 drop of methyl orange were added. Twenty per cent NaOAc was then added until all the rose-orange color disappeared. The mixture was heated to about 70° C., and two 5-ml. portions of 4 per cent $(NH_4)_2C_2O_4 \cdot H_2O$ were added slowly with stirring. After digestion for about an hour the precipitate ($BaSO_4$ and $CaC_2O_4$) was filtered and washed with warm water. The $CaC_2O_4$ was dissolved in 50 ml. of approximately 1 per cent $H_2SO_4$, heated to 80–90° C., and titrated with 0.025 $N$ $KMnO_4$

The cation-adsorption capacity was determined by leaching the Ba-soil with 100 ml. of 0.05 $N$ HCl. To a 25-ml. aliquot contained in a beaker, 20 ml. of ethanol, 1 drop of methyl orange, sufficient $N$ triethanolamine to neutralize the excess acid, and a measured amount of 0.05 $N$ $K_2SO_4$ in excess of the Ba present were added. The solution was then vigorously mixed with a mechanical stirrer, about 150 mgm. tetrahydroxyquinone and a few drops of 10 per cent $AgNO_3$ were added, and the excess $K_2SO_4$ was back-titrated with 0.05 $N$ $BaCl_2$ buffered to pH 8.1 with triethanolamine (17).

*Barium chloride-triethanolamine procedure.* The amounts of soil and the procedures for leaching and for the determination of Ca used were identical to those described under the barium acetate procedure. Exchangeable H and cation-adsorption capacity were measured by a modification of the procedure described previously (17). The modified method was as follows: To 25 ml. of the leachate obtained after treatment of the soil with the $BaCl_2$ buffer solution, 2 drops of 0.1 per cent solution of methyl orange and 25 ml. of reference solution were added. The reference solution consisted of 0.05 $N$ HCl and 0.1 $N$ $K_2SO_4$ and was standardized against the extracting solution which, after dilution with an equal volume of $H_2O$, was 0.05 $N$ in terms of OH and 0.1 $N$ in terms of Ba. The excess HCl

was back-titrated with a 0.05 $N$ BaCl$_2$-triethanolamine buffer (17), a mechanical stirrer being used. This titer, corresponding to the exchangeable H in the sample, was recorded. Consistent and vigorous stirring was maintained, and 10 ml. of ethanol, 10 drops of 10 per cent of AgNO$_3$, and about 150 mgm. of tetrahydroxyquinone were added, and the titration with the Ba buffer was continued until the excess sulfate ions had reacted to form BaSO$_4$ as indicated by a permanent rose color of the suspension. The total titer was equivalent to the exchange capacity per aliquot.

This method was found to give satisfactory results for most of the systems studied. It was noted, however, that with colloids of the 2:1 lattice type, the cation-adsorption capacity tended to decrease as the degree of Ca saturation increased, and, under these conditions, the sum of the exchangeable Ca and H was greater than the amount of Ba adsorbed by the colloids. Whenever this condition existed the sum of the exchangeable Ca and H was taken as the cation-exchange capacity rather than the Ba adsorbed as determied by difference.[3]

## RESULTS AND DISCUSSION

### Identification of saturation point by the CO$_2$ equilibration and the NH$_4$OH volatilization methods

With the CO$_2$ equilibration method of Bradfield and Allison the point of saturation can be interpreted on the basis of: (a) the difference between the total Ca added and the sum of CaCO$_3$ and Ca(HCO$_3$)$_2$; (b) the difference between the total Ca added and the Ca in solution at the initial constant pH; (c) the measurement of the specific conductivity; and (d) the sum of exchangeable Ca and that added at the initial constant pH. The first approach is considered by the originators of the method to be the most accurate. The last method is used by Naftel (22) for determining the "Ca-sorption capacity." In the present investigation all these criteria have been considered and the results compared.

The applicability of these possibilities are illustrated by the results with White Store shown in figure 1. Above the initial constant pH the exchangeable Ca is constant, the excess Ca being present as Ca(HCO$_3$)$_2$ and CaCO$_3$. Saturation is obtained just before the initial constant pH. This is shown by the specific conductivity curve. It is also indicated by the curve relating the percentage of Ca removed from solution to the total amount of Ca added. At the intersection of the highest specific conductivity measurement, the soil is saturated and probably contains only an excess of Ca(HCO$_3$)$_2$. The total milliequivalents of cations held adsorbed is designated as "cation-adsorption capacity," and the

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[3] It has since been found that reduced adsorption of Ba was due to the competition of the triethanolamine, which is preferentially adsorbed by the 2:1 lattice type of colloids. It did not interfere in the case of the Perrine soil and the permutite previously studied (18). Subsequent results with other soils have shown that the effect is largely restricted to systems of the 2:1 lattice type of colloids. By leaching a soil first with 50 ml. of the BaCl$_2$-triethanoimine buffer (for the purpose of obtaining the exchangeable H) and then with 50 ml. of 0.2 $N$ BaCl$_2$, this interference is eliminated and satisfactory results are obtained.

relative distribution of the cations is expressed as percentage saturation of a group or individual cations.

The results of measuring the point of saturation with the NH₄OH procedure are presented in figure 2.    The data show that the adsorption of NH₄ approaches
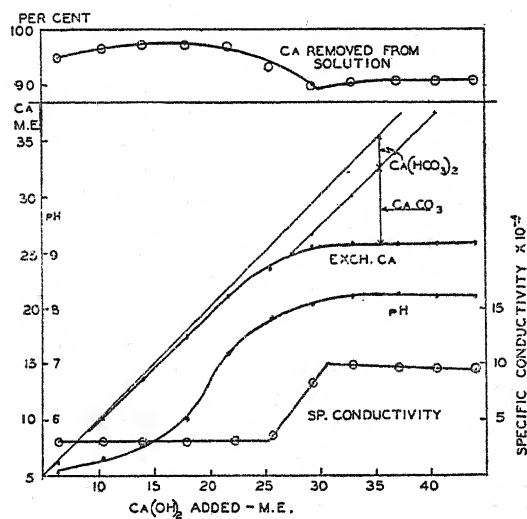


FIG. 1. THE SATURATION POINT OF WHITE STORE INTERPRETED ON THE BASIS OF
pH, SPECIFIC CONDUCTIVITY, AND PERCENTAGE OF TOTAL ADDED Ca
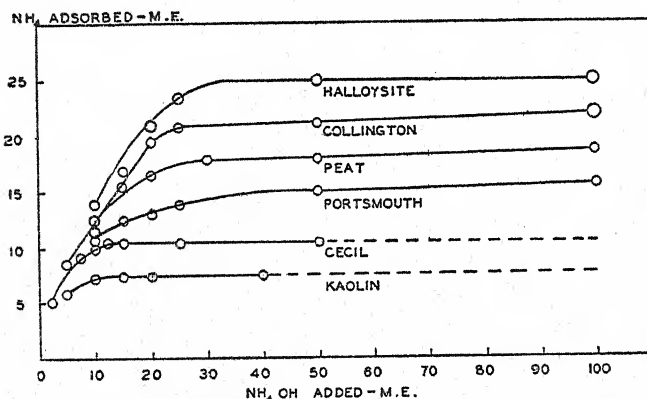REMOVED FROM SOLUTION



FIG. 2. ADSORPTION OF NH₄ FROM NH₄OH BY DIFFERENT SOILS AND MINERALS
The values for peat are on the basis of 10 gm.; all others on the basis of 100 gm.

a constant value with a relatively small excess of NH₄OH.    This is particularly true for the mineral colloids, whereas with the organic soils a greater excess of NH₄OH did not give a definite constant value.    The results pertaining to the constancy of the saturation point are essentially in agreement with those of Howard (14), Di Gleria and Kotzmann (11), Puri (25), and the unpublished data

of Keenen and O'Leary,[2] who also found the amounts of $NH_4$ adsorbed to be constant when soils were supplied with excess concentrations of urea (uramon) and following a 10-day incubation period.

### Comparison of methods for obtaining the cation-adsorption capacity

For the determination of the cation-adsorption capacity of soil the acetates of $NH_4$ and Ba are very widely used. Low values are usually obtained on highly unsaturated soils unless large excesses of the salts are used. Kelley (15) recommends, therefore, that such soils first be treated with a base. High values are believed by some (23, 24, 26) to be obtained on saturated soils containing free $CaCO_3$, particularly if a divalent salt is used for replacement. In the present study, samples were available which varied widely in the degree of saturation and in the amounts of $CaCO_3$.

The results with $NH_4OAc$ and $BaCl_2$-triethanolamine showed that the caton-adsorption capacity was not appreciably affected by the degree of Ca saturation or the presence of $CaCO_3$. Values determined by BaOAc were not significantly influenced by Ca levels below saturation but increased consistently in the presence of increasing amounts of $CaCO_3$. The reason for this greater adsorption is probably due to the interaction of the Ba salt with the $CaCO_3$ on the principle shown by Burgess and Breazeale (9) and by Tiurin (31). The extent to which basic salts (6) may have been formed has not been investigated.

In the comparison of methods for measuring cation-adsorption capacity the average of all Ca levels, including those containing $CaCO_3$, were recorded for both the $NH_4OAc$ and $BaCl_2$ buffer methods. With the BaOAc method, the average of the results from Ca levels of less than 100 per cent saturaton were taken. These data, together with those of the $CO_2$ equilibration and $NH_4OH$ volatilization methods, are presented in table 1.

Inspection of the data reveals a relatively good agreement among all methods with the hydrous-mica and the 2:1 lattice type of colloids. The $NH_4OAc$ method, however, yields lower results, particularly with systems that are essentially organic and with the 1:1 lattice type. The "Ca-sorption capacity," interpreted according to Naftel (22), is consistently high. The results also show good agreement of the cation-adsorption capacity, whether determined by the residual carbonate procedure or whether it is obtained by the difference of the Ca supplied and the Ca in solution, at the point of saturation (fig. 1). Finally, it will be noticed that the values for the organic and the 1:1 lattice type systems are somewhat lower with BaOAc than with the $BaCl_2$-triethanolamine.

The difference in the results of the equilibration method at reactions between pH 8.2 and 8.5 and, of the $NH_4OAc$ method at pH 7.0, is probably most readily interpreted on the basis of variations in the titration curves of the systems used. Using a divalent base, colloids of the 2:1 lattice type (relatively strong acids) appear saturated at about pH 7.0 (2, 5, 7, 16, 20), and adsorption of cations is practically constant above pH 6.0 (27). The titration curves of montmorillonite and hydrous mica are rather similar (16). In addition, the hydrous mica

is particularly strongly buffered at reactions below pH 6.0 (28). Hence, little difference in the cation-adsorption capacity may be expected between pH 7 and 8.2.

Titration curves of the 1:1 lattice type indicate that they are not saturated until a pH of 8 to 10 is obtained (5, 18, 21) and cations continue to be adsorbed with increasing pH (27). Systems of this type are only about 60 to 90 per cent saturated at pH 7.0 (16, 21). The lower values obtained by the $NH_4OAc$ method are in about the same proportion, with the halloysite having the greater effect. Such variations may be expected since the inflection point of the titration curve occurs at different pH levels for different members of the 1:1 lattice type (21).

### TABLE 1

*Cation-adsorption capacity of soils and minerals as measured by different methods*

| SOIL OR MINERAL | NATURE OF COLLOID PREDOMINANTLY | $CO_2$ EQUILIBRATION | | $NH_4OH$ | BaOAc‡ | $BaCl_2$- BUFFER | $NH_4OAc$ | "Ca- SORP- TION CAPA- CITY" (22) |
|---|---|---|---|---|---|---|---|---|
| | | A* | B† | | | | | |
| | | m.e. | m.e. | m.e. | m.e. | m.e. | m.e. | m.e. |
| Bentonite............... | 2:1 | 90.5 | 88.8 | 91.8 | 89.0 | 88.0 | 91.0 | 93.6 |
| White Store............. | 2:1 | 26.0 | 25.8 | 26.4 | 26.9 | 25.7 | 25.9 | 28.3 |
| Putnam.................. | 2:1 | 63.6 | 61.9 | .... | 62.3 | 63.3 | 60.3 | 69.8 |
| Illite................... | Hydrous mica | 20.4 | 20.4 | 19.4 | 19.7 | 19.1 | 18.8 | 23.2 |
| Collington.............. | Hydrous mica | 24.8 | 24.6 | 25.4 | 24.5 | 24.5 | 23.6 | 28.4 |
| Halloysite.............. | 1:1 | 25.1 | 24.8 | 24.8 | 21.8 | 23.2 | 15.6 | 31.2 |
| Kaolin.................. | 1:1 | 7.8 | 8.0 | 7.7 | 7.8 | 8.2 | 7.2 | 9.4 |
| Cecil................... | 1:1 | 12.6 | 11.9 | 13.4 | 11.2 | 13.3 | 9.7 | 15.4 |
| Durham................. | 1:1 | 13.5 | 12.9 | 13.8 | 13.6 | 14.5 | 10.8 | 16.1 |
| Portsmouth A........... | Organic | 19.2 | 20.0 | 18.4 | 19.4 | 19.0 | 11.6 | 22.6 |
| Peat.................... | Organic | 240.0 | 243.0 | 224.0 | 212.0 | 238.0 | 170.0 | 268.0 |

* From the residual carbonate.
† From the difference of Ca supplied and Ca in solution at the saturation point.
‡ Average values from samples containing no $CaCO_3$.

Direct titration of organic soils or colloids has, in general, failed to yield a definite saturation point. This is undoubtedly due in part to the fact that organic soils are highly buffered between pH 6 and 8.5 (4). Using a wide ratio of organic colloid and base, Feustel (12) succeeded in obtaining a break in the titration curve between pH 7.5 and 8.5. Titrating with triethanolamine and NaOH in the presence of $BaCl_2$, Mehlich (18) found the saturation point of a humic acid preparation at about pH 6, of a Florida peat at pH 7, and of a North Carolina muck at about pH 8.4. The $NH_4OH$ volatilization method, however, yields a saturation point which approaches a constant. This value is, however, generally higher than that obtained by titrating with a monovalent base to pH 7. For example, Anderson and Byers (1) found that the amount of NaOH required to obtain pH 7 was only 29 to 87 per cent of the capacity of the organic soils to adsorb $NH_4$ from $NH_4OH$. On the other hand, adsorption of divalent cations

at pH 7 is appreciably greater (3, 13). Results obtained by Bartlett and Norman (3), on the adsorption of $NH_4$ and Ba from their acetates by oat straw and its residue after decomposition, are of particular interest in this connection. They found that oat straw adsorbed 19.4 m.e. of Ba and 6.6 m.e. of $NH_4$, but after extraction of some of the soluble materials with hot water, adsorption was only 6.8 m.e. of Ba and 2.5 m.e. of $NH_4$. Following 6 months of decomposition, the oat straw residue adsorbed 95.8 m.e. of Ba and 46.3 of $NH_4$ before, and 40.0 m.e. of Ba and 19.2 m.e. of $NH_4$ after hot water extraction. These figures show: (a) that the amount of Ba adsorbed after extraction with hot water is about equivalent to the amount of $NH_4$ adsorbed before; and (b) that the relative differences in the amounts of $NH_4$ and Ba adsorbed were not affected by the hot water treatment. These results show that solubility of organic fractions

TABLE 2

*Cation-adsorption capacity and residual exchangeable H of Portsmouth-B as determined by different methods*

| SATURATING AGENT | REPLACING AGENT | CATION DETERMINED | CATION ADSORPTION CAPACITY | RESIDUAL EXCHANGE-ABLE H‖ |
|---|---|---|---|---|
| | | | *m.e.* | *m.e.* |
| $BaCl_2$-buffer* | $CaCl_2$ | $Ba^{++}$ | 21.4 | 0.0 |
| CaOAc* | $NH_4OAc$ | $Ca^{++}$ | 20.9 | 1.1 |
| $NH_4OAc$† | CaOAc | $NH_4^+$ | 13.8 | 6.2 |
| $NH_4OAc$‡ | $BaCl_2$-buffer | $NH_4^+$ | 20.4 | 0.8 |
| $NH_4OAc$§ | Direct distillation | $NH_4^+$ | 16.8 | 3.2 |

* Washed with $H_2O$.

† Washed with 80 per cent ethanol.

‡ Washed with 0.025 $N$ $NH_4OH$ in 80 per cent ethanol, excess $NH_4OH$ determined by back-titrating to pH 8.

§ As above, but excess $NH_4OH$ allowed to volatilize at 40° C.

‖ Determined with $BaCl_2$-buffer at pH 8.1 on parallel series of samples after saturation with $Ca^{++}$ or $NH_4^+$ and washing.

accounts in part for the differences in the amounts of Ba and $NH_4$ adsorbed. The fact, however, that the hot water treatment reduced the adsorption of both $NH_4$ and Ba to the same degree indicates that other factors play a dominant role. This problem was further investigated with an organic soil, on which different methods of procedure, shown in detail in table 2, were used.

The results show that the number of milliequivalents of $NH_4$ adsorbed is less than the number of milliequivalents of Ca replaced, but adsorption of both is nearly the same when the system is saturated with $NH_4OH$ to pH 8. The results also show that the residual H of the Ca-saturated system increased from 1.1 m.e. to 6.2 m.e. following the replacement of Ca by neutral $NH_4OAc$. If, however, the $NH_4OAc$-treated soil was washed with 0.025 $N$ $NH_4OH$ in 80 per cent alcohol and the excess $NH_4OH$ determined by back-titrating to pH 8, the cation-adsorption capacity and residual H were virtually the same as those obtained with CaOAc.

*Comparison of methods for obtaining the degree of saturation and exchangeable H*

The effect of the nature of the colloid on the cation-adsorption capacity, as obtained by different methods, may be expected to influence the exchangeable H or the degree of saturation. The relative significance of these differences due to the nature of the colloid is probably best illustrated by using a constant pH as a basis of comparison. Data in table 3 show the degree of saturation at pH 6 and 7 and the relative values when saturation by the equilibration method is taken as 100.

TABLE 3

*Percentage saturation of soils and minerals as measured by different methods*

| METHOD | SOIL OR MINERAL | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | White Store | Putnam | Illite | Halloy-site | Cecil | Durham | Ports-mouth | Peat |
| *Percentage saturation at pH 6* | | | | | | | | |
| Equilibration | 72 | 60 | 69 | 32 | 36 | 53 | 41 | 60 |
| BaCl$_2$-buffer | 71 | 60 | 73 | 34 | 34 | 50 | 41 | 61 |
| BaOAc | 68 | 61 | 71 | 37 | 40 | 53 | 40 | 68 |
| NH$_4$OH | 72 | .. | 72 | 33 | 34 | 52 | 43 | 65 |
| NH$_4$OAc | 71 | 63 | 74 | 51 | 46 | 67 | 67 | 85 |
| *Percentage saturation at pH 7* | | | | | | | | |
| Equilibration | 82 | 75 | 82 | 46 | 59 | 65 | 66 | 73 |
| BaCl$_2$-buffer | 82 | 76 | 88 | 50 | 56 | 61 | 67 | 74 |
| BaOAc | 79 | 77 | 85 | 53 | 67 | 65 | 65 | 83 |
| NH$_4$OH | 81 | .. | 87 | 47 | 56 | 64 | 69 | 79 |
| NH$_4$OAc | 82 | 80 | 89 | 74 | 77 | 81 | 109 | 103 |
| *Relative values — saturation by equilibration method = 100* | | | | | | | | |
| Equilibration | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| BaCl$_2$-buffer | 101 | 100 | 107 | 108 | 95 | 93 | 101 | 101 |
| BaOAc | 97 | 102 | 104 | 115 | 113 | 99 | 99 | 113 |
| NH$_4$OH | 98 | .. | 105 | 101 | 94 | 101 | 104 | 107 |
| NH$_4$OAc | 100 | 105 | 108 | 161 | 130 | 125 | 165 | 141 |

The effect of the nature of the colloid on the degree of saturation at pH 6 and 7 is rather pronounced. Illite, Putnam, and White Store are invariably more highly saturated than the minerals and soils of the 1:1 lattice type or of the organic soils. There is no significant difference among methods for White Store, Putnam, and illite. The variations are not very great for the other systems except those obtained with NH$_4$OAc, which are higher in every instance. At pH 7 the relative amounts of NH$_4$ adsorbed from NH$_4$OAc are about equal to the numer of milliequivalents of metal cations present in the organic soils, but are from 11 to 26 per cent greater than the amounts present in mineral soils.

The data in table 4 show the influence of the nature of the soil colloid on the relative efficiency of the NH$_4$ and Ba ions for obtaining the exchangeable H.

The results indicate that the relative efficiency of the neutral acetates in replacing H was appreciably less than that of the BaCl₂-triethanolamine buffer, particularly with samples of the organic and the 1:1 mineral lattice types. Although the values obtained with the BaCl₂-buffer are somewhat lower than those

TABLE 4

*Percentage exchangeable H of soils and minerals as measured by different methods*

| METHOD | SOIL OR MINERAL | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | White Store | Putnam | Illite | Halloy-site | Cecil | Durham | Ports-mouth | Peat |
| *Percentage exchangeable H at pH 6* | | | | | | | | |
| Equilibration..................... | 28 | 40 | 31 | 68 | 64 | 47 | 59 | 40 |
| BaCl₂-buffer..................... | 16 | 30 | 25 | 69 | 60 | 41 | 47 | 35 |
| BaOAc......................... | 7 | 28 | 9 | 39 | 34 | 18 | 18 | 21 |
| NH₄OAc......................... | 3 | 30 | 8 | 45 | 39 | 23 | 26 | 29 |
| *Percentage exchangeable H at pH 7* | | | | | | | | |
| Equilibration..................... | 18 | 25 | 18 | 54 | 41 | 35 | 34 | 27 |
| BaCl₂-buffer..................... | 8 | 16 | 13 | 43 | 45 | 31 | 30 | 24 |
| BaOAc......................... | 1 | 6 | 2 | 15 | 13 | 7 | 11 | 10 |
| NH₄OAc......................... | 0 | 6 | 0 | 23 | 15 | 14 | 7 | 5 |

TABLE 5

*Exchangeable H of soils as obtained by the BaCl₂-triethanolamine and the NH₄OH methods*

| SOIL NUMBER* | EXCHANGEABLE H | | SOIL NUMBER | EXCHANGEABLE H | |
|---|---|---|---|---|---|
| | BaCl₂-triethanol-amine method | NH₄OH method | | BaCl₂-triethanol-amine method | NH₄OH method |
| | *m.e.* | *m.e.* | | *m.e.* | *m.e.* |
| 198 | 1.3 | 2.6 | 103 | 4.4 | 4.2 |
| 14 | 1.6 | 1.5 | 188 | 5.4 | 5.5 |
| 48 | 1.6 | 1.6 | 87 | 5.5 | 5.7 |
| 33 | 1.6 | 1.7 | 205 | 6.2 | 6.4 |
| 34 | 2.4 | 2.3 | 203 | 7.4 | 7.3 |
| 200 | 2.5 | 3.1 | 204 | 10.8 | 10.4 |
| 86 | 2.8 | 2.3 | 202 | 15.2 | 15.0 |
| 80 | 2.8 | 2.4 | 208 | 18.8 | 19.8 |
| 201 | 4.1 | 4.6 | 207 | 21.5 | 22.6 |
| 16 | 4.2 | 3.6 | 206 | 140.0 | 136.0 |

* The analytical data of the soils with numbers smaller than 200 were made available through the courtesy of Dr. F. G. Keenen of the Du Pont Laboratories.

obtained by the equilibration method, the agreement is, in general, fairly good. The exchangeable H of different soils, replaced by the BaCl₂-buffer, is also closely correlated with the amounts of NH₄OH adsorbed, as is shown by the results in table 5.

*Efficiency of NH₄ and Ba in replacing Ca in relation to nature of colloid and degree of saturation*

The data pertaining to the efficiency of $NH_4$ and Ba in replacing Ca from the soils and minerals are shown in figures 3 and 4 and in table 6. They show the following principal facts: (*a*) Normal $NH_4OAc$ replaces all the adsorbed Ca and renders soluble virtually all the $CaCO_4$ in the systems studied; (*b*) 0.1 $N$ $NH_4OAc$ effectively replaces the adsorbed Ca from the mineral colloids but ineffectively

TABLE 6

*Efficiency of NH₄ and Ba salts in replacing Ca in relation to degree of saturation*

| Ca IN SOIL | | Ca REPLACED BY | | | | Ca IN SOIL | | Ca REPLACED BY | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Per cent saturation | | NH₄OAc | | BaOAc | BaCl₂-buffer | Per cent saturation | | NH₄OAc | | BaOAc | BaCl₂-buffer |
| | | 1 N | 0.1 N | | | | | 1 N | 0.1 N | | |
| | m.e. | m.e. | m.e. | m.e. | m.e. | | m.e. | m.e. | m.e. | m.e. | m.e. |
| *Putnam* | | | | | | *Halloysite* | | | | | |
| 44.2 | 28.1 | 28.5 | 28.3 | 28.4 | 27.5 | 14.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 |
| 60.4 | 38.4 | 38.3 | 37.2 | 38.2 | 38.0 | 22.3 | 5.6 | 5.4 | 5.5 | 5.6 | 5.5 |
| 75.3 | 47.9 | 47.8 | 47.3 | 47.4 | 47.0 | 45.4 | 11.4 | 11.5 | 10.7 | 10.6 | 11.2 |
| 87.1 | 55.4 | 55.3 | 55.0 | 55.0 | 54.6 | 60.2 | 15.1 | 14.8 | 14.8 | 14.2 | 14.2 |
| 100.0 | 63.8 | 63.8 | 63.2 | 59.5 | 62.9 | 87.3 | 21.9 | 21.8 | 20.5 | 19.7 | 20.4 |
| 115.5 | 73.5 | 72.4 | 68.8 | 59.5 | 63.4 | 100.0 | 25.1 | 25.1 | 23.5 | 22.2 | 22.3 |
| | | | | | | 113.5 | 28.5 | 27.9 | 26.6 | 25.0 | 25.8 |
| | | | | | | 127.8 | 32.1 | 32.1 | 29.4 | 25.8 | 27.0 |
| *Portsmouth* | | | | | | *Durham* | | | | | |
| 9.9 | 1.9 | 1.9 | 1.5 | 1.8 | 1.9 | 22.2 | 3.0 | 3.0 | 2.9 | 2.9 | 2.9 |
| 23.4 | 4.5 | 4.3 | 3.7 | 4.1 | 4.2 | 42.2 | 5.7 | 5.6 | 5.7 | 5.6 | 5.7 |
| 40.1 | 7.7 | 7.7 | 5.6 | 6.7 | 6.8 | 57.8 | 7.8 | 7.7 | 7.7 | 7.5 | 7.7 |
| 65.6 | 12.6 | 12.4 | 8.5 | 11.9 | 11.9 | 68.9 | 9.3 | 9.3 | 9.1 | 8.8 | 9.0 |
| 90.6 | 17.4 | 17.3 | 12.0 | 16.0 | 16.1 | 83.0 | 11.2 | 10.9 | 10.9 | 9.7 | 10.4 |
| 105.0 | 20.2 | 19.3 | 12.7 | 18.1 | 18.1 | 108.2 | 14.6 | 14.6 | 14.6 | 12.4 | 13.4 |
| 122.8 | 23.6 | 22.5 | 13.5 | 18.6 | 18.6 | 121.5 | 16.4 | 16.5 | 16.4 | 13.2 | 14.1 |
| 140.0 | 26.9 | 26.0 | 15.9 | 19.6 | 19.7 | 137.0 | 18.5 | 18.3 | 18.1 | 13.9 | 14.2 |
| 155.6 | 29.9 | 28.8 | 16.7 | 20.3 | 20.4 | | | | | | |
| 170.7 | 32.8 | 30.5 | 19.9 | 20.4 | 20.4 | | | | | | |

from the organic soils, particularly in the presence of $CaCO_3$; appreciable amounts of $CaCO_3$ are brought into solution with the mineral colloids; (*c*) both of the 0.2 $N$ Ba salts used replace adsorbed Ca effectively from all the soils and minerals studied. With increasing concentrations of $CaCO_3$, small but relatively constant amounts of Ca are brought into solution.

The efficiency of the replacement of Ca with 0.1 $N$ $NH_4OAc$ and with the 0.2 $N$ Ba salts permits direct comparison, since the amounts of soil or materials were used to give between 0.25 and 0.5 m.e. cations for leaching wih the $NH_4$ salts and between 0.5 and 1.0 me. cations with the Ba salts. Since 50 ml. was used

for all the leachings, a total of 5 m.e. of cations was supplied, or an excess of 10 to 20 times the symmetry concentration. The symmetry concentration of $N$ $NH_4OAc$ was, therefore, between 100 and 200. In the light of these considerations, the relative efficiency of the Ba and $NH_4$ ions to replace Ca is of appreciable
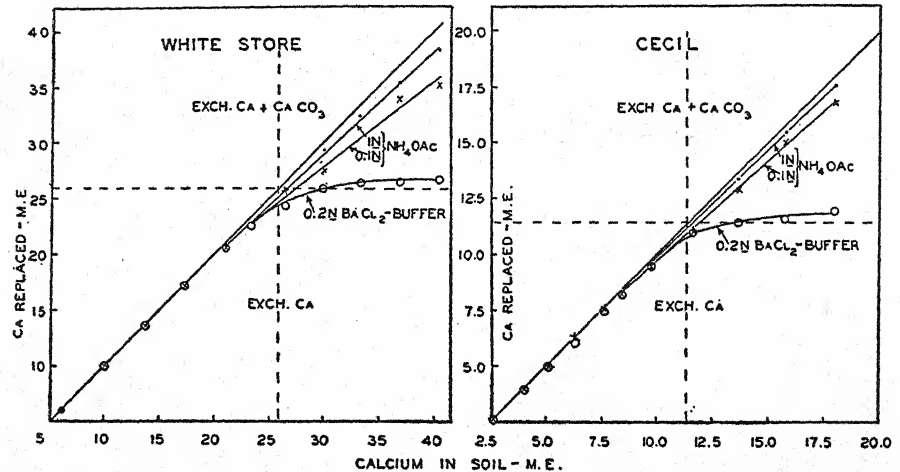


FIG. 3. RELATIVE EFFICIENCY OF $NH_4$ AND Ba SALTS IN REPLACING Ca FROM WHITE STORE AND CECIL SOILS
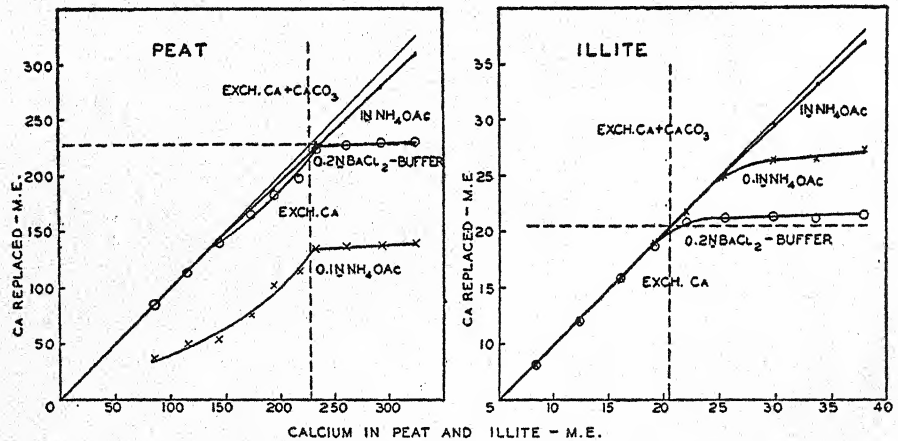


FIG. 4. RELATIVE EFFICIENCY OF $NH_4$ AND Ba SALTS IN REPLACING Ca FROM PEAT AND ILLITE

importance in the selection of methods for measuring the cation-exchange properties of soils, particularly those containing $CaCO_3$.

The $NH_4OAc$ method is frequently used to measure the cation status of soils following lime and fertilizer treatments. On the basis of the present results it appears, however, that the rate of reactivity cannot be correctly ascertained unless supplemented by other criteria. This point may be illustrated by the

results of a liming study presented in table 7. As a result of $CO_2$ equilibration the pH was substantially increased, indicating the probability that the samples contained residual $CaCO_3$. This was substantiated by a comparison of the exchangeable Ca and H found by the $BaCl_2$-buffer method before and after equilibration. The results also show that the $NH_4OAc$ method fails to differentiate between Ca that is exchangeable and that present as $CaCO_3$.

TABLE 7

*Effect of $CO_2$ equilibration on pH and exchangeable Ca of a limed soil (Portsmouth B) as measured by the $NH_4OAc$ and $BaCl_2$-buffer methods*

| | TREATMENT OF SOILS* | | | |
| | 5 tons $CaCO_3$ added | | 10 tons $CaCO_3$ added | |
| SOIL PROPERTIES MEASURED | Equilibration | | Equilibration | |
| | Before | After | Before | After |
|---|---|---|---|---|
| pH............................................. | 5.40 | 5.98 | 6.85 | 8.02 |
| Exchangeable Ca—$NH_4OAc$ method.........m.e. | 10.20 | 9.70 | 21.40 | 20.90 |
| Exchangeable Ca—$BaCl_2$-buffer method......m.e. | 8.40 | 9.60 | 16.50 | 21.10 |
| Exchangeable H—$BaCl_2$-buffer method.......m.e. | 11.70 | 9.50 | 3.90 | 1.50 |

* $CaCO_3$ as c.p. added on August 10, 1943. Sample taken for analysis on April 1, 1944.

TABLE 8

*Effect of additions of dolomite on the cation-exchange status of Portsmouth B soil as measured by the $NH_4OAc$ and the $BaCl_2$-buffer methods*

| SOIL NUM- BER | TREATMENT | pH | NH₄OAc | | | BaCl₂-BUFFER | | | |
| | | | Exch. cap. | Ca | Mg | Exch. cap. | H | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|
| | | | m.e. | m.e. | m.e. | m.e. | m.e. | m.e. | m.e. |
| 1 | None | 4.25 | 12.6 | 2.64 | 0.60 | 22.0 | 15.2 | 2.60 | 0.52 |
| 1 | 2 tons dolomite* | .... | 12.4 | 4.39 | 1.68 | 21.6 | 15.0 | 2.88 | 0.58 |
| 2 | None | 5.40 | 13.8 | 10.20 | 0.68 | 21.2 | 11.7 | 8.40 | 0.54 |
| 2 | 2 tons dolomite | .... | 14.2 | 12.05 | 1.92 | 21.6 | 11.4 | 8.92 | 0.56 |
| 3 | None | 6.85 | 12.6 | 21.40 | 0.60 | 20.2 | 3.9 | 16.50 | 0.48 |
| 3 | 2 tons dolomite | .... | 12.8 | 23.25 | 1.56 | 19.6 | 3.8 | 16.90 | 0.58 |

* The 2 tons of dolomite used supplied 2.25 m.e. Ca and 2.40 m.e. Mg on the basis of 100 gm. soil.

This problem was further investigated by adding the equivalent of 2 tons per acre of commercial dolomite to the soils varying in reaction between pH 4.25 and 6.85. Without premoistening of the treated samples, the cation-exchange properties were determined with the $N$ $NH_4OAc$ and $0.2$ $N$ $BaCl_2$-triethanolamine methods. The results given in table 8 show that $NH_4OAc$ removed very large, and the $BaCl_2$-buffer only small, amounts of Ca and Mg from the dolomite. Virtually the same quantities of Ca and Mg were rendered soluble at reactions between pH 4.25 and 6.85. Samples 2 and 3 were the same as those in table 7

before equilibration. A comparison of the amounts of Ca removed from sample 1 and from samples 2 and 3 shows that the $NH_4OAc$ rendered soluble, not only relatively constant amounts of Ca from the added dolomite, but also the total of the residual $CaCO_3$. The average sum of Ca and Mg rendered soluble from dolomite by $NH_4OAc$ and $BaCl_2$-triethanolamine is found to be 62 and 11 per cent, respectively.

On the basis of the results presented it may be concluded that base-exchange data obtained with the $NH_4OAc$ method must be interpreted with caution unless they are supported by supplementary data obtained by other methods. The following combinations of procedure recommend themselves. Determine replaceable cations with $NH_4OAc$, saturate with Ca or Ba for cation-exchange capacity, and measure exchangeable H by the $CO_2$ equilibration or the $NH_4OH$ volatilization methods. If the soil contains no free salts, the sum of the exchangeable cations should be equal to the cation-exchange capacity. With only soluble salts of monovalent bases present, the exchangeable H values should be the same whether determined by the $CO_2$ equilibration or the $NH_4OH$ methods. If, however, the soil contains divalent carbonates the cation-adsorption capacity will be equal to the sum of the metal cations and the H by $CO_2$ equilibration, but it will be greater if H is determined by $NH_4OH$. This is due to the fact that part of the carbonates, which as yet have not reacted with the exchangeable H of the soil, will be made to do so during $CO_2$ equilibration and thereby reduce the base required for saturation. On the other hand, $NH_4OH$ is capable of detecting the exchangeable H in the presence of the non-reacted carbonates or oxides of Ca and Mg. From this it is apparent that the true cation-exchange status in the presence of carbonates cannot be satisfactorily ascertained by the $NH_4OAc$ and the $CO_2$ equilibration methods. Yet, the degree to which soils containing carbonates remain unsaturated must be of appreciable importance in problems of soil development, nutrient conservation, and nutrient availability to plants.

For the proper evaluation of the cation-exchange status in these and related problems, the use of a buffer method involving a divalent cation appears more promising.

### SUMMARY

Soils and minerals representing the organic, hydrous mica, the 2:1 and 1:1 lattice type of colloids were used for:

A comparison of equilibration and $NH_4OH$ volatilization methods for determining the saturation point.

A comparison of the $CO_2$ equilibration, $NH_4OH$, $NH_4OAc$, $BaOAc$, and $BaCl_2$-triethanolamine methods for determining the cation-adsorption capacity and degree of saturation as influenced by the type of colloid.

A comparison of the relative efficiency of the $NH_4$ and Ba ions in replacing exchangeable Ca in the presence and absence of $CaCO_3$.

The following principal results were obtained:

The saturation point of the mineral colloid is very satisfactorily obtained by both the $CO_2$ equilibration and the $NH_4OH$ volatilization methods. With organic soils, the

$NH_4OH$ method yields values that are somewhat lower and less constant than those obtained with the equilibration procedure.

With colloids of the hydrous mica and the 2:1 lattice type, the cation-adsorption capacity was virtually the same with all the methods studied. The $NH_4OAc$ method yielded lower values with colloids of the organic and the 1:1 lattice type than those obtained by the other methods. An organic soil at first saturated with Ca contained greater amounts of H after treatment with $NH_4OAc$. More $NH_4$ ions remain adsorbed from $NH_4OH$ than from $NH_4OAc$. Adsorption of Ba from BaOAc was greater in the presence of $CaCO_3$ in all cases.

The saturation deficit in relation to pH and expressed as percentage saturation was virtually the same with all methods in the case of the hydrous mica and 2:1 type of colloids. With colloids of the 1:1 lattice type and the organic soils the degree of saturation was consistently higher when determined by the $NH_4OAc$ method.

The efficiency of the Ba and $NH_4$ ions in replacing Ca is about the same for the mineral colloids; it is appreciably less with $NH_4$, however, for the organic soils. Almost all the freshly precipitated $CaCO_3$ present in the various systems above pH 8 is soluble in 1 $N$ $NH_4OAc$ but is only slightly soluble in 0.2 $N$ BaOAc and 0.2 $N$ $BaCl_2$-triethanolamine.

Some of the errors arising from the presence of carbonates are discussed. It is concluded that a method employing a divalent cation buffered at about pH 8 is best adapted for the evaluation of the cation-exchange status of groups of soils with a variety of types of colloidal material.

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# DYNAMICS OF WIND EROSION: I. NATURE OF MOVEMENT OF SOIL BY WIND[1]

### W. S. CHEPIL[2]

*Canada Department of Agriculture*

The energy relationships between the air currents, commonly known as wind, and the soil are of great importance in the problem of wind erosion and its control. But, unfortunately, much of the information available in the past on the nature of air currents near the ground and on the importance of wind as a geologic agent in soil formation is too fragmentary and inadequate for wide application to the practical aspect of wind erosion control. Consequently, when research work on wind erosion of soil was begun at this laboratory, little aid was obtainable from the records of previous work, and it was found necessary to investigate the fundamental aspects of the problem, namely, the energy relationship between wind and soil.

The factors influencing wind erosion are numerous and hence add considerably to the complexity of the problem. The most important of these factors may be listed as follows:

I. Air
 1. Velocity
 2. Turbulence
 3. Density, affected by
  a. Temperature
  b. Pressure
  c. Humidity
 4. Viscosity

II. Ground
 1. Roughness
 2. Cover
 3. Obstructions
 4. Temperature
 5. Topographic features

III. Soil
 1. Structure, affected by
  a. Organic matter
  b. Lime content
  c. Texture
 2. Specific gravity
 3. Moisture content

It is evident that the wind erosion problem depends on the mutual relationship of a combination of many factors. The influence of any factor that is involved in any condition may be negative or positive with regard to erosion, and in fact, one factor may counteract the influence of another in virtually any situation. For example, although it has been found (4) that wind turbulence increases erosion, yet the degree of erosion of a rough surface, where turbulence is more developed, is much less than that of a smooth surface over which the mean velocity of wind is greater. In both cases it is the net effect of the two opposing trends which determines the actual amount of erosion of the soil. Thus, in order that any condition may be understood and properly interpreted, it is essential that the individual factors involved be known and their relative significance accurately evaluated.

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Briefly, the immediate problems for the soil conservationist are to determine the relative significance of the various factors influencing the movement of the soil material by the wind and to appreciate the physical nature of wind translocation. In order to answer some of the elementary questions connected with these problems, it was necessary to run a large series of experiments. The first of these had to do with the physical nature of soil drifting, the results of which are herewith reported.

## REVIEW OF LITERATURE

The movement of soil particles by the wind has been studied by a number of investigators. Free (6) asserted in his review of the literature on the problem up to 1911 that the largest proportion of the soil carried by the wind is moved in a series of short bounces called "saltation." He reported that sand never bounces high above the ground and in the desert cannot be felt by a person mounted on a camel. The smaller the soil particles, the greater is the influence of the wind upon it and the closer the approach of the path of saltation to a line parallel with the direction of the wind. The smallest quartz particles carried in saltation are about 0.1 mm. in diameter. Particles smaller than this have a velocity of fall lower than the upward velocity of the turbulent wind. Such particles are carried more or less parallel with the general direction of the wind, and form what has been termed a "suspension movement." They may be carried through the atmosphere for long periods of time and will fall to earth only with rain or after the wind has slackened considerably. Fine dust is thus often carried great distances from its original location.

In addition to flow in saltation and suspension, there is still another type of movement. Udden (7) observed that quartz grains larger than about 0.5 mm. in diameter and smaller than 1 mm. are too heavy to be transported through the air, but roll and slide along the surface of the ground. This type of movement is termed, by Bagnold (1), "surface creep." On the other hand, grains greater than 1 mm. in diameter are too large to be moved by ordinary erosive winds (5).

Although the manner of the transport of sand by wind was understood in a general way many years ago, it was not until recently that a comprehensive study was made by Bagnold (1). He asserted that dune sand is carried by wind mainly in saltation and surface creep and to a minor degree in true suspension. Bagnold concluded from theoretical calculations that with average dune sand the suspension flow, even under a relatively strong wind, does not exceed one twentieth of the flow in saltation and surface creep.

For arable soils, the only information available is a preliminary report from this laboratory (2), concerning the proportion of soil carried in different types of movement. Chepil and Milne (3) made measurements of the relative amounts of soil carried by wind over cultivated fields. The soil catchers used at that time were satisfactory for measuring rate of flow in saltation and surface creep, but were not entirely effective in trapping fine dust carried in suspension. It was observed that much soil was moved in saltation, but a very substantial proportion constituting the finest fraction was carried in true suspension.

In addition to information on the general mechanism of transport of soil by wind, data are herewith presented on the relative proportion of different types of movement on different soils with varying degrees of roughness of surface, and on the relative nature and intensity of soil movement as influenced by some of the major types of tillage treatments.

## EXPERIMENTAL PROCEDURE

In the development of experimental technique to study the quantity of soil transported by wind, it was found necessary to recognize the fundamental differences that exist between the transport of particles by saltation and surface creep and by movement in suspension. A fine grain of quartz dune sand when shot into the air at a speed of 9 miles per hour travels 20 cm. before its speed is reduced 50 per cent. Because of this continuing and directed motion, the rate of the flow of particles by saltation is determined easily by trapping the particles in narrow containers, open to windward. On the other hand, the measurement of the movement of fine dust is rather more complicated, for such particles are seriously affected by the wind's internal movements, that is, by the
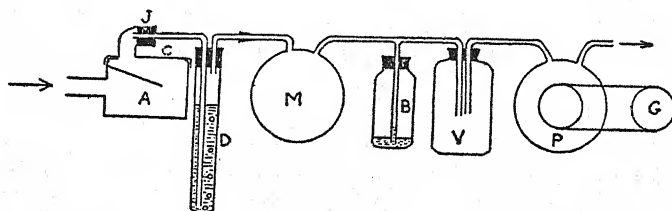


FIG. 1. DIAGRAMMATIC REPRESENTATION OF APPARATUS USED FOR MEASURING QUANTITIES OF SOIL CARRIED IN SALTATION AND SUSPENSION

continued and instantaneous changes in its velocity and direction. Consequently, small particles do not enter the volume of still air contained in the trap, but instead are deflected from it and carried along with moving air. The procedure for measuring the rate of suspension flow is therefore much more complicated. In the first place, the volume of air in which dust is suspended must be determined accurately, and in the second, the dust itself must be filtered off completely and removed into a receptacle in which it may be weighed.

The method used in measuring the quantity of soil moving in saltation and suspension is indicated diagrammatically in figure 1. Soil material carried by the wind enters a narrow box $A$ through a rectangular nozzle, $\frac{1}{2}$ inch wide and 2 inches high, facing into the wind. The particles carried in saltation are trapped in the box and may be removed and weighed after detachment of $A$ from the rest of the apparatus at a stoppered joint $J$ and removal of a tight-fitting cover $C$. The particles in suspension, however, are carried into the trap by suction created by a vacuum pump $P$ and collected in a 6-inch column of distilled water in cylinder $D$. Air intake through the apparatus is measured with a gas meter $M$ and its volume corrected on the basis of atmospheric pressure with the

aid of a mercury barometer $B$.   More than one dust-catching unit can be con-
nected by rubber tubing to a vacuum flask $V$.   This type of arrangement facil-
itates simultaneous measurement of soil flow at various positions.   The vacuum
pump was driven by a small gasoline motor at $G$.

The amount of dust trapped was determined by evaporating the water and
weighing the residue.   The relative concentration of particles carried in sus-
pension at any height was determined by dividing the weight of the residue
by the corrected volume of filtered air.   Suspension flow was determined by
multiplying concentration per unit volume by velocity of the wind.   This was
done on the assumption that the velocity of particles carried in suspension was
equal to that of the wind.   Photographs and indirect measurements substanti-
ated this assumption.

In addition to measurements of soil flow at different heights, the total amounts
of soil carried in different types of movement were determined.   Total saltation
and surface creep were determined by the method of Bagnold (1), and the sus-
pension flow was ascertained by subtracting the flow in saltation and surface
creep from the total flow as determined by the difference in the weight of thor-
oughly air-dry soil before and after exposure to an erosive wind.   These measure-
ments were made both in the open field and in a portable field tunnel, described
previously (2), and on different types of soil with varying degrees of roughness
of surface.

In order to determine the nature of soil movement under different conditions
of soil and wind, photographs were taken of the paths of moving soil particles.
Sunlight admitted vertically through a lens in the ceiling of a darkened wind
tunnel was used for illumination.   The lens was 25 cm. long and 12 cm. wide
and had a focal length of approximately 2 feet.   It produced a very intense
vertical beam of light, which illuminated an area, 25 cm. long and 1 cm. wide,
parallel with the direction of the wind.   Particles flying through the illuminated
space reflected light distinctly, and their paths appeared on a photographic
plate as silvery threads, or as a series of dots or dashes against a black back-
ground.   Photographic exposures of $\frac{1}{25}$ and $\frac{1}{10}$ of a second were made for the
purpose of indicating the shape and length of grain paths and $\frac{1}{100}$ and $\frac{1}{50}$ of a
second for determining the speed of the grains through the air.

<div align="center">RESULTS</div>

<div align="center">*Nature of wind translocation*</div>

Photographs and direct visual observation indicated that all soils were carried
by wind in the three types of movement already mentioned.   The relative
proportion of each type of movement varied greatly for different soils.

The greatest proportion of the movement in all cases examined was by par-
ticles in saltation.   After being rolled by the wind, the particles suddenly
leaped almost vertically to form the initial stage of the movement in saltation.
Some grains rose only a short distance, others leaped 1 foot or more, depending
directly on the initial velocity of rise from the ground.   They also gained con-
siderable forward momentum from the pressure of the wind acting upon them,

and acceleration of horizontal velocity continued from the time grains began to rise to the time they struck the ground. In spite of this acceleration, the grains descended in almost a straight line invariably at an angle between 6 and 12 degrees from the horizontal. On striking the surface they either rebounded and continued their movement in saltation, or lost most of their energy by striking other grains, causing these to rise upward and themselves sinking into the surface or forming part of the movement in surface creep. Irrespective of whether the movement was initiated by impact of descending particles or by impact of rolling grains, the initial rise of a grain in saltation was generally in a vertical direction.

The cause of this vertical rise was not at all apparent. It was found that soil grains jumped vertically off a smooth surface, such as a wooden floor, after rolling for as short a distance as 2 cm., although there were neither soil grains nor other obstructions against which they could strike and rebound into the air. The probable cause of the vertical rise was thought to be a direct impact of a facet of an irregularly shaped grain against the tunnel floor. From a theoretical point of view, however, if no other impact forces are involved, the angle with which a descending grain would rebound from a smooth horizontal surface should be equal to the angle of descent, which was 6 to 12 degrees. Actually, the angle of ascent was between 75 and 90 degrees in the majority of cases. This seemed incredible unless it was presumed that the vertical rise was due to some force other than the force of impact of the grain against the surface.

The only logical explanation of the vertical rise of particles in saltation appears be by the theory of the Bernoulli effect. This effect is apparently due to two causes, the spinning of the grains and the steep velocity gradient near the ground. Actual photographs, some of which are shown in figures 2 and 3, indicate that grains carried in saltation rotate at a speed of 200 to 1,000 revolutions per second. The photographs show clearly that about 50 per cent of the grains carried in saltation are spinning, while another 25 per cent exhibit relatively indistinct rotation. It is possible, however, that more than 75 per cent of the grains were rotating but that this could not be indicated without greater intensity of illumination. Nor was it possible to indicate rotation for grains approaching a spherical shape, since photographs merely show the variation in the intensity with which the reflecting facets of the grain were illuminated. The more angular the grain, the more distinctly rotation appeared on the plate.

On account of a rapid clockwise spinning of the grain, the air near the grain surface is carried around it. On the lower side, assuming the wind to be traveling from left to right, this air is moving against the direction of the wind; on the upper side, it moves with it. The velocity of the air at any point near the grain is thus made up of two components, one due to the wind and the other to the spinning of the grain. On the upper side these components have the same direction, whereas below they have opposite directions. Thus, the velocity is greater at the top surface than at the bottom, and according to the Bernoulli theorem, the pressure is decreased at the top and increased at the bottom, and so the grain tends to rise.

The Bernoulli effect is further intensified by virtue of the fact that a steep velocity gradient exists near the ground. At a threshold wind velocity, that is,
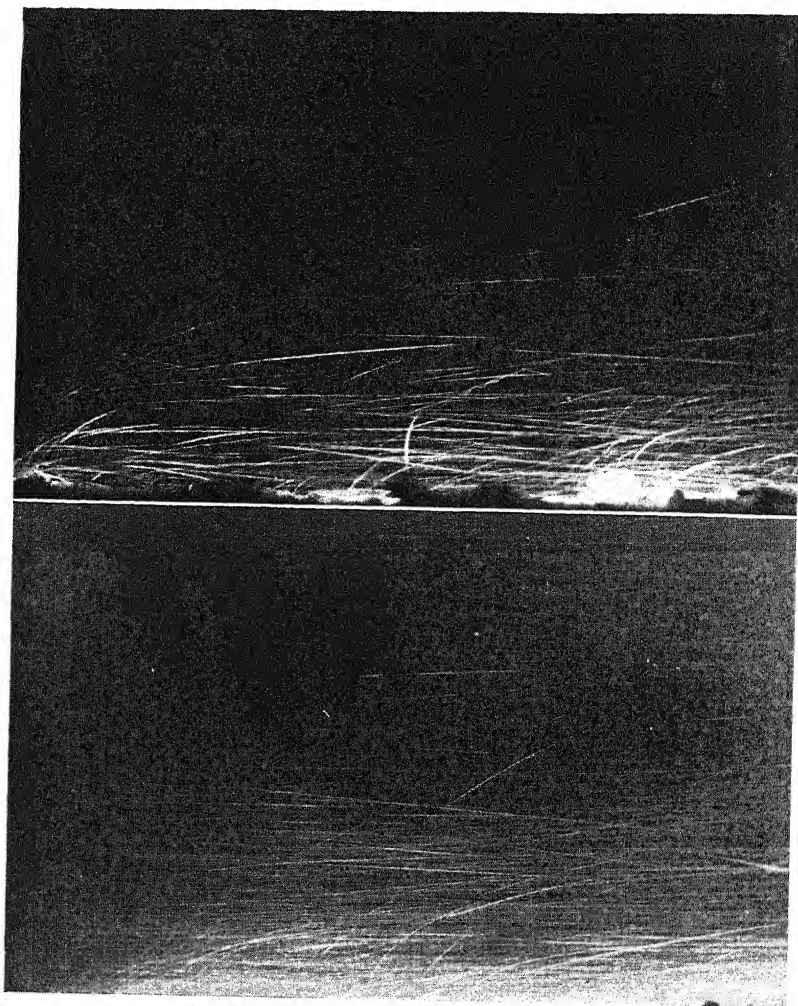


FIG. 2. PHOTOGRAPHS OF PATHS OF WIND-BORNE SOIL PARTICLES, INDICATING MOVEMENT IN SALTATION AND SUSPENSION OVER A LEVEL SURFACE OF (TOP) SCEPTRE HEAVY CLAY AND (BOTTOM) HATTON FINE SANDY LOAM

a velocity just high enough to initiate the movement in saltation, the following is a typical case of average velocities encountered near a smooth ground surface:

| Height, *mm* | 0.02 | 0.1 | 0.2 | 0.3 | 0.6 | 0.9 | 1.2 | 1.5 | 1.8 |
|---|---|---|---|---|---|---|---|---|---|
| Velocity, *cm./sec.* | 0 | 104 | 152 | 189 | 234 | 254 | 272 | 297 | 304 |

The variation in air velocity near the ground causes a substantially higher rate of air flow at the upper than the lower surface of the grain of, say, 0.2 mm.

in diameter, and this difference in velocity may be expected to produce a similar and additive effect to that caused by the spinning of the grain in a current of air. Consequently, if the total difference in the pressure between the upper and the lower surfaces is greater than the force of gravity acting downward, the grain will rise in a vertical direction.



FIG. 3. PHOTOGRAPHS OF PATHS OF WIND-BORNE SOIL PARTICLES, INDICATING (TOP) MOVEMENT IN SALTATION AND SUSPENSION OVER A LEVEL SURFACE OF HAVERHILL LOAM, (BOTTOM) MOVEMENT IN SUSPENSION OVER A RIDGED SURFACE

As no experimental data are available concerning a sphere the size of a sand grain spinning in an air current near the ground, it is impossible to confirm the existence of a vertical component of wind force as postulated above. Experiments are now being undertaken to obtain definite information on this problem.

After being shot into the air, the grains rose to various heights and, because of force of gravity, fell at an accelerating velocity. There was at the time a horizontal acceleration of the falling particle due to the forward pressure of the

wind upon it. Photographs indicate that the downward and the forward accelerations were approximately equal, and the inclined path of the falling grain was therefore almost a straight line. Only a slight curvature downward was observed in most cases. The angle of descent varied but little and, as already pointed out, was between 6 and 12 degrees from the horizontal. Smaller grains descended at a somewhat smaller angle than the larger grains. The angle of descent did not vary greatly with wind velocity, but the higher the wind the greater the height to which some grains rose in the air, and hence the corresponding longer average path.
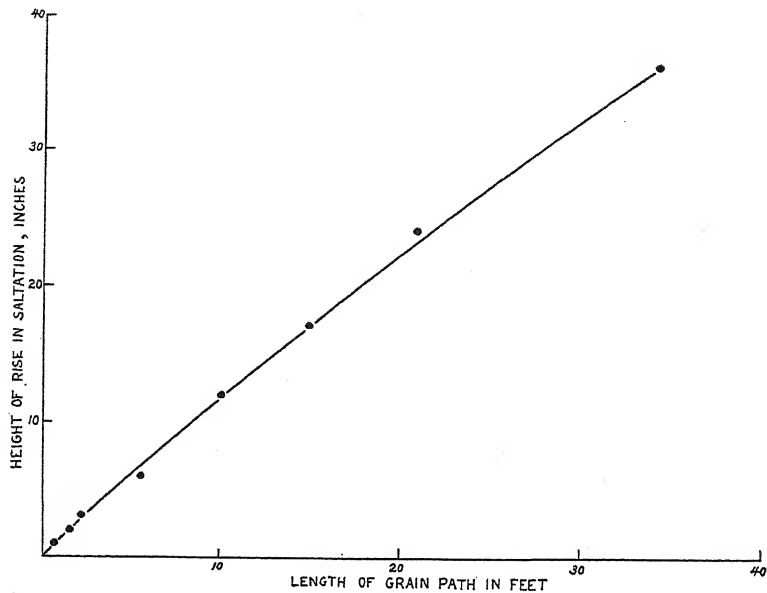


FIG. 4. RELATION OF HEIGHT OF RISE IN SALTATION TO LENGTH OF GRAIN PATH (HORIZONTAL PLANE)

On the whole, the horizontal distance through which the grain continued to rise was about one fifth to one fourth of the total horizontal length of a single leap in saltation.

On a smooth surface consisting only of erosive grains, there was a remarkable consistency in the shape of grain paths. The shape of the paths was much less regular over a rough surface, but the general character of the movement in saltation remained the same. Irrespective of the degree of surface roughness, a close relationship existed between the average height to which the grains rose in the air and the horizontal length of grain leap. This relation is indicated in figure 4. The ratio of height of rise to the horizontal equivalent of length of grain leap was about 1:7 for a rise up to 2 inches in height, 1:8 for a rise of 2 to 4 inches, 1:9 for 4 to 6 inches, and 1:10 for heights above 6 inches. The results were the same for all soils used in the investigation.

The surface creep of soil grains could not be recorded photographically but

was plainly visible to the naked eye. The grains in surface creep were too heavy to be moved by the direct pressure of the wind, but derived their kinetic energy from the impacts of smaller grains moving in saltation. Grains in saltation, on the other hand, received most of their impact energy from the direct pressure of the wind. It is evident that the movement of soil by wind is dependent, not so much on the force of the wind acting on the surface of the ground, as on the velocity distribution to such height as the grains rise in saltation. This height is definitely limited, and it may be concluded, therefore, that wind erosion is mainly a surface phenomenon and is not directly dependent on the condition of the wind above that restricted distance.

### Movement of dust in suspension

The results of measurements made in the open field showed that the mechanism of transport of soil by wind is very similar to that of dune sand described by Bagnold (1), except that in addition to movement in saltation and surface creep there was, in some cases, a substantial proportion of the soil carried in true suspension. The presence of fine dust, even in very appreciable amounts, did not seem to affect the nature of the movement in saltation or surface creep, but it greatly influenced both the threshold wind velocity and the intensity of erosion for a given wind (5).

Once lifted off the ground, the particles in suspension were completely borne up by the wind. In the open country they usually reach great heights and do not fall to the ground except with rain or after the wind has slackened considerably.

The mechanism by which fine dust is lifted off the ground is entirely different from that of saltation. A previous study (5) showed that samples of soil composed only of fine dust particles were extremely resistant to erosion by wind. In fact, quartz particles less than 0.05 mm. in diameter could not be moved by wind velocities as high as 37 miles per hour at a 6-inch height. In mixtures with coarser grains ranging up to 0.5 mm., however, these particles moved readily, and the threshold velocity of the mixtures was lowered very considerably. It may be said, therefore, that movement of fine dust in an air current is mainly the result of movement of grains in saltation; hence, without saltation movement, dust clouds would not arise, except on a relatively limited scale as a result of disturbance by moving vehicles, animals, etc.

The relative quantities of fine dust particles blown off different soils are indicated in figures 2 and 3. The suspension flow, though clearly visible to the naked eye, is indicated by very faint lines on a photographic plate. The difficulty is attributed to the relatively small diameter of the particles and to their high speed, which is approximately that of the wind. A very sensitive film and light much brighter than sunlight are essential for a clear indication of suspension flow.

In spite of these difficulties, the relative concentration of suspended dust is plainly indicated for different types of soil. Photographs indicate almost no suspension flow over Sceptre heavy clay, an appreciable concentration over

Hatton fine sandy loam, and a concentration so dense over Haverhill loam as to mask the appearance of movement in saltation. Wind velocity in all cases was about 17 miles per hour at a 12-inch height.

In contrast to the movement of grains in saltation, the movement of fine dust in suspension, after it has been lifted off the ground, is completely governed by the characteristic movement of the wind. The influence of an eddy on suspended dust is indicated clearly in the lower photograph of figure 3, which was taken at the time of a gentle movement of air following a stronger wind that initiated the movement of saltation. The back-eddy of air currents is shown

TABLE 1

*Relative quantities of soil carried in surface creep and saltation under different conditions of surface roughness and wind*

| WIND VELOCITY AT 12-INCH HEIGHT | SOIL TYPE | SMOOTH SURFACE | | | | | | | RIDGED SURFACE* | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Surface creep | Saltation carried below the height of | | | | | | Surface creep | Saltation carried below the height of | | | | | |
| | | | 1 inch | 3 inches | 6 inches | 12 inches | 24 inches | 36 inches | | 1 inch | 3 inches | 6 inches | 12 inches | 24 inches | 36 inches |
| m.p.h. | | mgm./cm. width/sec. | per cent | per cent | per cent | per cent | per cent | per cent | mgm./cm. width/sec. | per cent | per cent | per cent | per cent | per cent | per cent |
| 17 | Sceptre heavy clay | 15.9 | 27 | 66 | 91 | 98 | .... | .... | 1.9 | 20 | 54 | 74 | 96 | 99+ | .... |
| | Haverhill loam | 3.1 | 24 | 63 | 86 | 97 | 99+ | .... | 0.4 | 18 | 47 | 72 | 95 | 99+ | .... |
| | Hatton fine sandy loam | 2.8 | 30 | 65 | 88 | 98 | 99+ | .... | 0.5 | 21 | 50 | 75 | 97 | 99+ | .... |
| 25 | Sceptre heavy clay | 142.1 | 28 | 56 | 77 | 91 | 99 | 99+ | 4.5 | 25 | 55 | 76 | 93 | 98 | 99+ |
| | Haverhill loam | 9.2 | 24 | 54 | 75 | 90 | 97 | 99+ | 1.2 | 18 | 45 | 72 | 95 | 98 | 99+ |
| | Hatton fine sandy loam | 3.3 | 29 | 63 | 83 | 95 | 99 | 99+ | 0.6 | 20 | 47 | 73 | 95 | 99 | 99+ |

* Ridges were 2.5 inches high, 9 inches wide, running at right angles to the wind.

plainly by the characteristic paths of suspended particles and almost duplicates a diagrammatic representation of wind structure previously recorded over the same type of surface with the aid of sensitive oscillating plates (4).

### Concentration of wind-borne particles at different heights

Measurements of the concentration of wind-borne particles in a portable field tunnel and also in the open field indicated that most of the soil movement in saltation was carried below the height of 2 or 3 feet. In fact, over 90 per cent of the soil was transported below the height of 12 inches, and this was found to be true for several widely different soils chosen for investigation.

The results of this study obtained in the open field under various conditions of soil, wind velocity, and surface roughness are given in table 1. In general, the movement in saltation was the same on all soil types investigated, but some variation was found in the proportion of grains carried at different heights.

Coarsely granulated soils, such as Sceptre heavy clay, drifted closer to the ground than the more pulverized Haverhill loam, but the difference was not appreciable.

There were large differences in the rate of surface creep, which was particularly high on coarsely granulated Sceptre heavy clay and least on finely granulated Hatton fine sandy loam. Roughly, the amount of surface creep depended on the quantity of erosive grains greater than 0.5 mm. in diameter for cultivated soils and over 0.25 mm. for dune sand.

The relative concentration of wind-borne particles at different heights above a rough surface differed widely from that above a smooth one. Figures 5 and 6 show typical differences in relative concentration of drifting soil over the two
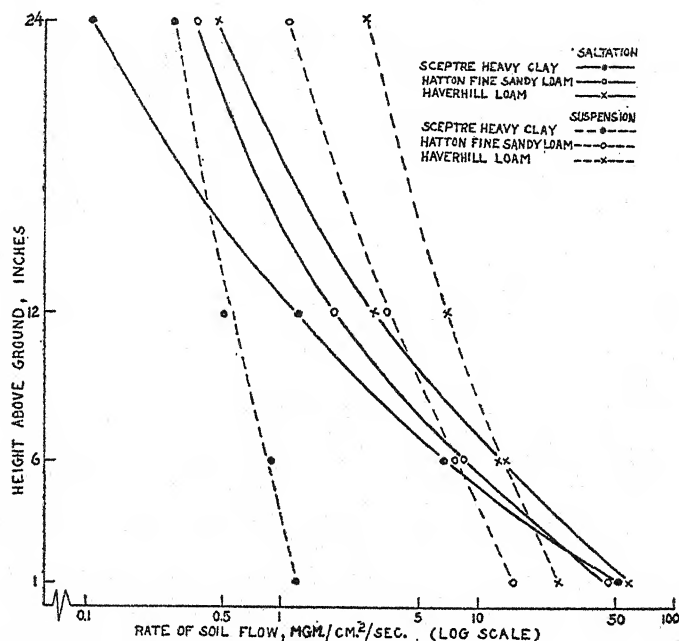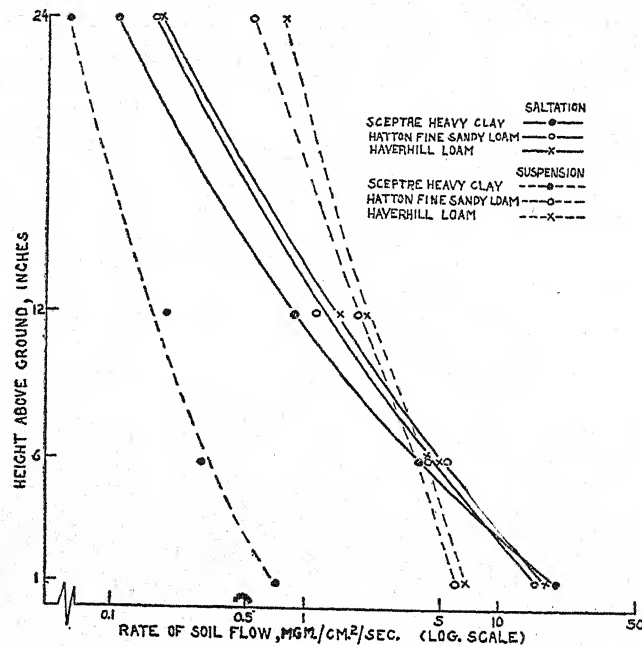


FIG. 5. DISTRIBUTION OF WIND-BORNE PARTICLES CARRIED IN SALTATION AND SUSPENSION AT DIFFERENT HEIGHTS ABOVE A SMOOTH SURFACE

types of surface—wind velocity in both cases being the same at 12-inch height. The ridges had a marked effect on lowering the total rate of soil flow and virtually eliminated surface creep. Furthermore, many of the coarser granules that moved in saltation over a smooth surface were apparently trapped by the ridges, thus lowering appreciably the relative concentration of particles near the ground.

The relative concentration of soil particles at different heights remained the same under a wide range of wind velocity; hence the graphs presented in figures 5 and 6 give only averages for a range of wind velocity from 13 to 30 miles per hour at 12-inch height. The data show that the ratio of saltation to suspension decreased rapidly with height above the ground, as would be exacted. As Grains in saltation do not generally rise higher than several feet above the

ground, the soil carried above this height is in true suspension and capable of being carried to great heights and over long distances from the original location.

Figures 5 and 6 indicate further that virtually a straight-line relationship exists between height and the logarithm of the rate of flow in saltation and suspension over all soils investigated. There seems to be some functional relationship between the rate of soil flow and height, for nearly all of the experimental values fall very closely to curves of the same characteristic shape.



FIG. 6. DISTRIBUTION OF WIND-BORNE PARTICLES CARRIED IN SALTATION AND SUSPENSION AT DIFFERENT HEIGHTS ABOVE A RIDGED SURFACE

## Proportion of different types of flow on different soils

The relative rates of soil transport in each of three types of movement varied widely on different soils (table 2). The proportion moved in surface creep constituted 7 to 25 per cent of the total flow, the lowest rate being on highly pulverized Haverhill loam, the highest on coarsely granulated Sceptre heavy clay. Flow in saltation varied much the same way as surface creep and composed 55 to 72 per cent of the total flow, depending on soil type. The proportion of flow in suspension constituted about 3 per cent of the total flow on Sceptre heavy clay and as much as 38 per cent on typically dusty Haverhill loam and was approximately equal to the proportion of particles smaller than 0.1 mm. found in the soil. The data in table 2 indicate that some particles larger than 0.1 mm. must have been carried in suspension, probably those of lowest specific gravity. As the percentage of particles smaller than 0.15 mm. in all soils was substantially

greater than the percentage carried in suspension, it is evident that only a small proportion of the size above 0.1 mm. was carried in true suspension.

There was a constant proportion of the three types of flow throughout the wide range of wind velocity used in the investigation, and on this account the values in table 2 indicate only the average results obtained for many individual cases. Measurements were made on a level surface on which the surface projections in the form of clods and surface ripples did not exceed 0.75 inch in height.

TABLE 2

*Relative proportion of three types of flow on different soils**

| SOIL TYPE | SOIL REMOVED IN | | |
|---|---|---|---|
| | Saltation | Suspension | Surface creep |
| | *per cent* | *per cent* | *per cent* |
| Sceptre heavy clay...................... | 71.9 | 3.2 | 24.9 |
| Haverhill loam......................... | 54.5 | 38.1 | 7.4 |
| Hatton fine sandy loam................. | 54.7 | 32.6 | 12.7 |
| Fine dune sand........................ | 67.7 | 16.6 | 15.7 |

\* The size distribution of erosive grains in the soils was as follows:

| SIZE OF PARTICLES.......................... mm. | DISTRIBUTION OF PARTICLES | | | | |
|---|---|---|---|---|---|
| | 0.83–0.42 | 0.42–0.25 | 0.25–0.15 | 0.15–0.1 | 0.1 |
| | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Sceptre heavy clay.................... | 33.5 | 46.1 | 14.9 | 4.0 | 1.5 |
| Haverhill loam....................... | 13.3 | 17.3 | 15.1 | .22.3 | 32.0 |
| Hatton fine sandy loam................ | 1.1 | 6.0 | 26.4 | 40.5 | 26.0 |
| Fine dune sand....................... | 0.1 | 2.1 | 54.2 | 35.6 | 8.0 |

Increasing the roughness of surface caused a proportional reduction in the rate of movement in surface creep. A rough surface, such as that composed of cultivator ridges extending at right angles to the direction of wind, trapped most of the surface creep but failed to reduce the movement in saltation and suspension to quite the same degree.

### Relative efficiency of cultural treatments in trapping drifting soil

The data in table 2 give some idea of the relative amounts of soil that are carried away by the winds. Dust in suspension is transported far and wide; hence the regions in which it is deposited benefit but little in the way of additional soil, but the much more limited eroded area loses a great deal. In saltation and surface creep, on the other hand, soil is not usually carried far and is deposited in or near the vicinity of the affected area. Many cultural and cropping methods are devised to trap the grains in saltation and surface creep to prevent the spread of erosion to surrounding unaffected areas. It has been pointed out that surface creep may be almost eliminated and saltation greatly

reduced as a result of ridging a highly erosive soil. The higher the ridges the more effective they are in stopping surface creep and saltation, but as movement in suspension and surface creep is dependent wholly on movement in saltation, the elimination of saltation will eliminate all other forms of movement. The whole program of wind erosion control is therefore based on reduction or elimination of movement in saltation.

Soil ridges may be used to reduce or eliminate saltation. It is often preferable to ridge the whole of the affected area, but this treatment is not always possible, and ridging narrow strips at regular intervals across the field is often resorted to. Stubble and crop strips may be used for a similar purpose.

The width of trap strip that may be required depends partly on the length of jump of grain in saltation and partly on the trapping capacity or receptiveness of the surface. Standing grain stubble is probably the most effective form of trap, for it will trap all the soil moving into it in saltation. It can therefore be considered as fully receptive. The minimum width of stubble strip, however, would have to be not less than the maximum horizontal length of a single leap of the grain in saltation. The data in table 1 and figure 4 combined supply complete information on the approximate percentage of soil grains that may be trapped by any width of a wholly receptive trap strip.

Thus, supposing the width of a strip of short stubble to be 10 feet, figure 4 indicates that to jump this distance the grain in saltation would have to rise to a height of approximately 12 inches. Furthermore, it is indicated in table 1 that between 90 and 98 per cent of the flow in saltation is below this height; hence a 10-foot strip of short stubble may be expected to trap between 90 and 98 per cent of the flow in saltation, depending on soil type and wind velocity. It can be found in like manner that a 2-foot stubble strip will trap about 50 per cent of the flow in saltation and a 30-foot strip over 99 per cent. These values corroborate the results obtained from actual practice in the field.

The data indicate further that the effectiveness of a trap varies somewhat with wind velocity. Thus, it is shown that in order to trap 99 per cent of the movement in saltation a 20-foot strip of totally receptive surface would be required for a 17-mile-per-hour wind, and a 35-foot strip for a 25-mile-per-hour wind.

There are other angles to be considered in deciding on the width of trap strip that would be most effective. The next of these considerations is the height of the stubble. A 3-foot width of 6-inch stubble, for example, will trap on an average about 85 per cent of the total flow in saltation, but a 3-inch stubble will trap about 60 per cent.

The minimum width of trap required depends also on the capacity to hold the blown soil. Long stubble, in addition to being more effective in trapping the encroaching drift, has a greater holding capacity. Other factors being equal, the holding capacity varies directly with the height of the stubble. The effectiveness of the trap is reduced to zero as soon as the trap has reached its holding capacity. Hence, to be fully effective, the minimum width should be that required to store the encroaching drift, plus that width to leeward that will remain relatively free to act as an effective trap. The width that may be required

to store the encroaching drift cannot be estimated with any degree of accuracy, for the amount of erosion is dependent to a large measure on the conditions of the weather, which cannot be predicted. Hence, a considerable margin over and above the minimum requirement must be allowed.

Ridges were found to have a lower trapping capacity than the standing grain stubble, for many of the grains bounced off the ridges one or more times before they were finally trapped in the furrows. The trapping capacity of ridges depends on their size. Ridges 2.5 inches high and 9 inches wide were about 50 per cent as effective as a 6-inch wheat stubble, whereas cultivator ridges 5 inches high and 18 inches wide and lister furrows 12 inches deep were 77 to 83 per cent and 85 to 92 per cent as effective, respectively.

The foregoing results were obtained on a highly nonerosive clay soil that was exceedingly resistant to the grinding action of flying grains. Many soils do not exhibit such marked resistance, for the ridges may wear down rapidly and lose much of their sheltering effect. The trapping capacity of the grain stubble, on the other hand, is not at all affected by abrasion.

## CONCLUSIONS

Because of rapid spinning of the grains moving in saltation and a steep velocity gradient, there appears to be a considerable vertical component of wind force near the ground. On account of these effects the grains rise steeply and descend very obliquely toward the surface. As the downward acceleration, due to gravity, and the forward acceleration, due to wind pressure, are approximately equal, the grains fall in almost a straight line. They strike the surface at an angle of 6 to 12 degrees.

Movement in suspension and in surface creep is a result of movement in saltation. The whole program of wind erosion control should therefore depend on methods designed to reduce or eliminate saltation.

The intensity of soil movement depends not so much on the force of the wind acting on the ground, as on its pressure against the grains as they leap in saltation. Soil movement is therefore dependent not on velocity at any fixed height but on the velocity distribution to the height of saltation.

Dust in suspension does not affect the general character of the movement in saltation or in surface creep, but the presence of dust in the soil increases the minimum velocity required to initiate erosion and decreases the intensity of erosion for a given erosive wind. Once lifted off the ground, fine dust is carried to great heights and distances from its original location and thus may be considered a complete loss to the eroding area. The soil moved in saltation and surface creep, on the other hand, usually remains within the eroding area, especially when the erosive winds are from different directions. The maximum diameter of soil particles carried in suspension is on an average slightly greater than 0.1 mm.

The proportion of the three types of movement varies widely for different soils. In the cases examined, between 55 and 72 per cent of the weight of the soil was carried in saltation, 3 to 38 per cent in suspension, and 7 to 25 per cent in surface

creep.   Coarsely granulated soils erode mainly in saltation, and finely pulverized soils, in saltation and suspension.

The trapping capacity of stubble or ridged strips depends on the relative receptiveness of the surface and the length of jump of particles in saltation. The data presented supply information on the approximate percentage of soil grains that may be caught by trap strips of different widths.

The effectiveness of a particular type of trap depends also on the height and density of the obstructions and on the resistance of these obstructions to the abrasive action of wind-borne grains.   Soils vary greatly in resistance to abrasion, but grain stubble is virtually unaffected.

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# HYDROGEN-ION CONCENTRATION OF THE IMPORTANT SOILS OF THE UNITED STATES IN RELATION TO OTHER PROFILE CHARACTERISTICS: IV. AZONAL SOILS

ERNEST H. BAILEY[1]

*United States Department of Agriculture*

The hydrogen-ion concentrations of the zonal and intrazonal soils were discussed in previous papers (2, 3, 4). This paper deals with the hydrogen-ion concentration of azonal soils, of which two groups—the lithosols and alluvial soils—have been selected.

## LITHOSOLS

Table 28 shows some morphological characteristics of the lithosol (19, 40) profiles and their hydrogen-ion concentrations. Six series were selected as representative of this group—the Sumter, Lehew, Dekalb, Muskingum, Lehigh, and Underwood soils. In all of these series the A horizon is just beginning to form, but no B horizon has developed.

The Sumter series occurs largely associated with the Houston soils in the rendzina areas among the red and yellow podzolic soils, in Alabama, Mississippi, and eastern Texas. For the most part it is developing on the soft Selma chalk formation from which associated series have developed (2, fig. 1; 5; 10; 29; 37). It occupies the steeper slopes and occurs along drainage ways.

The Lehew series is found in the hilly to mountainous regions of Pennsylvania and West Virginia in the region of gray-brown podzolic soils. This soil is forming on shallow residual material chiefly from non-calcareous red sandstones with some shales (2, fig. 1; 16; 42; 44).

The Dekalb soils occur in the mountainous parts of New York, Pennsylvania, Maryland, and West Virginia in the podzol region. They are developing on thin residual material from noncalcareous gray to gray-brown sandstones and shales (2, fig. 1; 30; 34; 44).

The Muskingum soils are found in Indiana, Ohio, Kentucky, and Virginia in the gray-brown podzolic region. Like the Dekalb, this series is forming on shallow residual material from noncalcareous light or brownish gray sandstones and shales (2, fig. 1; 7; 31; 32). It differs from the Dekalb series in occupying lower elevations and, therefore, is forming under different climatic conditions.

The Lehigh series occurs in the mountainous areas of New Jersey, Pennsylvania, Maryland, and Virginia in the gray-brown podzolic soils region.

## TABLE 28
*Lithosols*

| PRO-FILE NUM-BER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 408 | *Sumter clay loam* Hale Co., Ala. | 0–5 | Dark gray friable clay | 8.2 |
| | | 5–14 | Grayish yellow crumbly friable clay with white and yellow flecks | 8.2 |
| | | 14–17 | Yellowish or creamy gray clay with some white flecks | 8.2 |
| | | 17+ | Parent material.  Gray firm chalk | 8.1 |
| 411 | *Sumter clay* Navarro Co., Tex. | 0–8 | Dark yellowish brown calcareous clay—granular structure | 8.0 |
| | | 8–30 | Greenish yellow calcareous clay | 8.4 |
| | | 30+ | Greenish yellow calcareous clay banded with bright yellow | 8.6 |
| 412 | Dallas Co., Ala. | 0–5 | Gray friable clay containing considerable organic matter | 8.2 |
| | | 5–11 | Speckled pale yellow and dark gray friable clay | 8.2 |
| | | 11–30 | Light grayish yellow friable clay | 8.2 |
| | | 30+ | Pale yellowish gray clay mottled with yellow friable material and partly decomposed Selma chalk | 8.1 |
| 413 | *Lehew gravelly fine sandy loam* Hampshire Co., W. Va. | 1–0 | Dark brown loamy leaf mold | 3.8 |
| | | 0–6 | Reddish brown friable gravelly fine sandy loam to gravelly very fine sandy loam | 4.5 |
| | | 6–24 | Indian-red friable loam, partly disintegrated shale and sandstone below | 4.7 |
| 414 | *Lehew stony loam* Pocahontas Co., W. Va. | 1–0 | Brown loamy leaf mold | 5.2 |
| | | 0–7 | Dark chocolate-reddish-brown friable loam | 4.0 |
| | | 7–34 | Dark Indian-reddish-brown loam | 4.3 |
| 415 | *Lehew stony silt loam* Wyoming Co., Pa. | 0–1 | Dark brownish red gravelly silt loam | 4.8 |
| | | 1–8 | Brownish red gravelly silt loam | 5.2 |
| | | 8–15 | Red gravelly silt loam on bedrock of reddish sandy shales | 5.3 |
| 416 | *Dekalb silt loam* Randolph Co., W. Va. | ½–0 | Partly decomposed organic matter | 5.1 |
| | | 0–½ | Yellowish gray silt loam containing considerable organic matter | 4.2 |
| | | ½–5 | Pale yellow silt loam | 4.4 |
| | | 5–17 | Light brownish yellow heavy silt loam or silty clay loam | 4.7 |
| | | 17–28 | Grayish yellow silty clay mottled brown and red with rotten shale fragments | 4.7 |

TABLE 28—*Continued*

| PRO-FILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 417 | *Dekalb stony loam* Lyocoming Co., Pa. | 1½–0 | Dark brown fibrous leaf mold | 3.6 |
| | | 0–1½ | Yellowish gray stony loam, shale fragments | 3.9 |
| | | 1½–12 | Pale yellow stony loam, shale fragments | 4.3 |
| | | 12–36 | Grayish yellow silty clay loam with rotten shale fragments | 4.5 |
| 418 | *Dekalb silt loam* Cattaraugus Co., N. Y. | 1–0 | Black decomposed leaf mold matted together by fine roots | 3.9 |
| | | 0–2 | Yellowish brown heavy silt loam—slight granulation | 4.3 |
| | | 2–8 | Yellow heavy silt loam, firm but not compact in place | 4.2 |
| | | 8–22 | Bright yellow heavy silt loam, firm and dense, rests on rock | 4.3 |
| 419 | *Muskingum silt loam* Muskingum Co., Ohio | 1–0 | Dark grayish brown layer consisting of partly decomposed organic matter | 5.6 |
| | | 0–5 | Brownish yellow silt loam | 5.2 |
| | | 5–12 | Yellow compact silty clay loam | 4.3 |
| | | 12+ | Partly weathered shales and sandstone | 4.1 |
| 420 | Belmont Co., Ohio | 0–3 | Gray silt loam | 4.7 |
| | | 3–8 | Pale yellow silt loam | 4.5 |
| | | 8–15 | Yellow silty clay loam | 4.7 |
| | | 15–34 | Yellow silty clay, and yellow and gray partly weathered shale | 4.5 |
| 421 | *Muskingum loam* Grayson Co., Va. | 1–0 | Grayish brown leaf mold | 3.8 |
| | | 0–6 | Light brown loam | 4.1 |
| | | 6–30 | Brownish yellow silty clay | 4.4 |
| | | 30+ | Yellow and red sandstone and shale and silty clay material | 4.6 |
| 422 | *Lehigh silty clay loam* Bucks Co., Ps. | 0–7 | Gray heavy silt loam with scattering of shale fragments through section | 5.5 |
| | | 7–12 | Brown silty clay mottled with yellow, brown, and purple | 4.8 |
| | | 12–23+ | Light purplish compact and indurated silty clay mottled with yellow and overlying thinly laminated shale | 5.7 .. |
| 423 | *Lehigh gravelly silt loam* Lancaster Co., Pa. | ½–0 | Dark grayish brown leaf mold | 3.9 |
| | | 0–3 | Dull blue or slaty gray friable silt loam, high content of shale fragments | 4.4 |
| | | 3–7½ | Dull bluish gray less friable silt loam with high percentage of shale fragments | 4.5 |
| | | 7½–18 | Dark bluish gray, heavy, compact, brittle silty clay loam with a high content of purplish material | 4.6 |

TABLE 28—*Continued*

| PRO-FILE NUM-BER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 423 | *Lehigh gravelly silt loam* | 18–40 | Dark grayish brown, compact, tough silty clay with a large percentage of bluish shale | 4.9 |
| | Lancaster Co., Pa.—*Cont'd.* | 40+ | Thin layer of yellowish brown to reddish mottled highly decomposed material on top of the weathered rock | 5.1 |
| 424 | *Lehigh silt loam* | 0–1 | Dark gray silt loam, includes leaf mold | 4.3 |
| | Orange Co., Va. | 1–8 | Light gray silt loam, some shale fragments | 4.5 |
| | | 8–20 | Dull yellowish gray friable granular clay, some shale fragments | 4.4 |
| | | 20–30 | Dark gray friable silty clay loam and rotten rock | 4.7 |
| | | 30+ | Dark gray to black graphitic shale | 4.9 |
| 425 | *Underwood silt loam* | 0–14 | Reddish brown silt loam | 5.6 |
| | | 14–30 | Reddish brown loam | 5.8 |
| | Benewah Co., Idaho | 30–42 | Dark yellowish brown clay loam | 5.8 |
| | | 42+ | Disintegrating basalt | 6.0 |
| 426 | *Underwood loam* | 0–12 | Yellowish brown loam containing numerous soft red pellets | 5.3 |
| | Yakima Indian Reservation, Wash. | 12–24 | Granular heavy reddish brown loam, fewer red pellets | 5.3 |
| | | 24–36 | Reddish brown granular clay loam, resting on disintegrating basalt | 5.7 |
| 427 | Yakima Indian Reservation, Wash. | 0–12 | Yellowish brown loam | 5.8 |
| | | 12–24 | Darker yellowish brown loam, disintegrating basalt below | 5.8 |

This soil is developing on shallow residual material from noncalcareous dark-colored shales (2, fig. 1; 6; 12; 15).

The Underwood soils occur in the humid portions of Washington, Idaho, Oregon, and northern California in the gray-brown podzolic and red podzolic soil regions. It is developing on residual material from basalt, the same parent material as that of the Olympic and Aiken series (2, fig. 1; 22; 25; 27; 33; 35; 41).

In general, the hydrogen-ion concentrations of these lithosol profiles are largely influenced by the nature of the parent material. For example, the Sumter series, which is developing on highly calcareous material, is alkaline throughout in all three profiles, although it occurs in a humid region where the normal soils are acid (3, tables 13, 14). The pH values of their profiles range from 8.0 to 8.6. This averages a trifle higher than that of the Houston, as one would expect (4, table 27). In like manner, the Underwood soils that are developing from residual material from basic igneous rocks average less acid than the Lehew, Dekalb, Muskingum, and Lehigh, which are developing on residual material

from noncalcareous shales.   The pH values of the Underwood profiles vary from 5.3 to 6.0, and those of the Lehew, Dekalb, Muskingum, and Lehigh profiles from 3.6 to 5.7.

## ALLUVIAL SOILS

The alluvial soils (40) have the widest distribution of any of the groups of soils throughout the United States.   Table 29 shows some of the physical characteristics of the alluvial soil profiles and their hydrogen-ion concentrations. Thirteen series were selected as representative of these soils.   They are the Stendal in the gray-brown podzolic soil regions; the Huntington, Sharkey, and Panther, from both the gray-brown and the red and yellow podzolic soils regions; the Verdigris, Lightning, and Osage from the prairie region; the Lamoure from both the prairie and chernozem regions; the Havre, Harlem, and Bowdoin from the chestnut soil region; the Billings from the desert soil regions; and the Holtville from the red desert soil region (2, fig. 1).    Although these soils occur under varying climatic conditions and are derived from different parent material, they have this point in common: because of their extreme youth, they have developed little or no soil profile.   The layers found are, to a large degree, merely differences in the parent material as laid down by the water.

The Stendal (28, 39) series occurs as imperfectly drained light-colored soil material of overflow bottoms from deep deposits of acid silts and clays from areas of sandstone, siltstone, shale, and loess.   It occurs in the southern part of Indiana.

The Huntington soils are well-drained first-bottom soils developing from materials washed from areas of limestone with some sandstone, siltstone, and shale material (17, 18, 24, 39).   They occur in southern Indiana, Kentucky, Tennessee, West Virginia, Virginia, Maryland, Pennsylvania, Ohio, Arkansas, and Missouri.

The Sharkey and Panther soils occur on poorly drained bottom lands in southern Indiana, Tennessee, Mississippi, Louisiana, Texas, and Missouri.   The heavy, fine-textured material forming them has been deposited by the large rivers such as the Mississippi, Missouri, Arkansas, and Ohio.   The soils are rather high in organic matter at the surface (1, 26).   The Panther series has not yet been correlated; therefore, its name is only tentative.   It was mapped as Sharkey but has been separated as a new series because it is acid instead of neutral to alkaline.

Although the Verdigris, Lightning, and Osage soils are found in the prairie region in eastern Kansas, western Missouri, eastern Oklahoma, and northwestern Arkansas, they were originally covered with deciduous forests (20, 21).   The Verdigris and Osage are fairly high in organic matter, but the Osage is more poorly drained than the Verdigris and has a higher organic matter content.   The Lightning series is slightly more poorly drained than the Osage but appears to be developing on material carried down from the lighter colored planosols of the region.   Hence, it is a light-colored soil (20).

The Lamoure series, found in the prairie and chernozem regions, is derived

### TABLE 29
*Alluvial Soils*

| PRO-FILE NUM-BER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 429 | *Stendal silt loam* Washington Co., Ind. | 0–2 | Grayish brown silt loam mottled with gray | 6.2 |
| | | 2–6 | Light grayish brown silt loam mottled with gray | 5.5 |
| | | 6–15 | Yellowish brown silt loam mottled with gray | 5.6 |
| | | 15–75 | Light gray silt loam stained with yellowish brown | 5.1 |
| | | 75–98 | Yellowish brown silt loam mottled with light gray | 5.5 |
| | | 98–135 | Yellowish brown silt loam mottled with light gray | 6.2 |
| | | 135–188 | Yellowish brown silt loam mottled with light gray | 6.6 |
| 430 | *Stendal silty clay loam* Pike Co., Ind. | 0–10 | Grayish brown plastic sticky silty clay loam highly mottled with iron | 4.7 |
| | | 10–18 | Mottled gray and yellow plastic stickly silty clay loam | 4.7 |
| | | 18–35 | More compact, tougher, mottled gray and yellow clay | 5.1 |
| | | 35–44+ | Dominantly light gray compact silty clay mottled with yellow | 6.4 |
| 431 | Washington Co., Ind. | 0–1½ | Light grayish brown silty clay loam mottled with gray | 5.9 |
| | | 1½–6 | Lighter grayish brown silty clay loam mottled with gray | 5.7 |
| | | 6–12 | Light grayish yellow silty clay loam mottled with gray | 5.6 |
| | | 12–24 | Cream-colored silty clay stained with light reddish yellow | 5.8 |
| | | 24–75 | Cream-colored silty clay mottled with light gray | 6.1 |
| | | 75–116 | Mottled reddish yellow and light yellowish gray silty clay | 7.8 |
| | | 116–172 | Yellow silty clay mottled with light gray | 7.8 |
| | | 172–198 | Light gray silty clay mottled with yellow | 7.6 |
| 433 | *Huntington silt loam* Augusta Co., Va. | 0–8 | Light brown silt loam | 7.7 |
| | | 8–28 | Dark brown silty clay loam | 7.9 |
| | | 28+ | Brown gravelly loam | 8.2 |
| 434 | Jefferson Co., Tenn. | 0–20 | Mellow yellowish brown heavy silt loam | 7.8 |
| | | 20–32 | Firm brown friable silt loam more yellow than surface | 8.1 |
| | | 32–40+ | Yellowish brown silt loam faintly mottled with yellow and drab | 8.0 |
| 435 | Mercer Co., Ky. | 0–8 | Light buff-brown to brown silt loam | 7.7 |
| | | 8–68 | Color gradually deepens to rich dark brown silt loam at 66 inches | 7.7 |

TABLE 29—*Continued*

| PRO-FILE NUM-BER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 439 | *Sharkey very fine sandy loam* St. Landry Parish, La. | 0–10 | Dark gray very fine sandy loam mottled with rusty brown | 6.7 |
| | | 10–16 | Mottled light gray and rusty brown very fine sandy loam | 7.5 |
| | | 16–24 | Mottled gray and rusty brown very fine sandy loam | 7.9 |
| | | 24–50 | Bluish gray and rusty brown silty clay | 7.5 |
| 441 | *Sharkey clay* Terrebonne Parish, La. | 0–6 | Very dark grayish brown clay | 5.9 |
| | | 10–24 | Gray to dark gray clay mottled with rust-brown | 7.1 |
| | | 48–80 | Blue-gray clay mottled with rust-brown | 7.1 |
| 442 | *Panther (tentative) silty clay loam* Livingston Parish, La. | 0–5 | Deep brown mucky silty clay loam, very slushy when wet | 4.5 |
| | | 5–17 | Brownish drab mottled with light bluish gray and rust brown | 4.5 |
| | | 17–33 | Drab clay faintly mottled with limonite yellow quite sticky when wet | 4.5 |
| | | 33–70 | Pale bluish gray silty clay with a yellowish green tint | 5.4 |
| 443 | *Panther (tentative) clay* Concordia Parish, La. | 0–1 | Very dark gray silty clay | 5.9 |
| | | 1–12 | Very dark bluish gray with a little yellow brown mottling heavy clay | 5.3 |
| | | 12–22 | Bluish gray heavy clay with yellow–brown mottling | 5.0 |
| | | 22–38 | Bluish gray mottled with yellow-brown plastic clay, black concretions | 5.3 |
| 444 | Sharkey Co., Miss. | 0–4 | Dark grayish brown, faint mottles of brown heavy clay | 6.2 |
| | | 4–22 | Dark bluish gray, mottled with rust-brown heavy waxy silty clay | 5.8 |
| | | 22–80 | Light gray mottled with rust-brown, heavy tough clay | 6.4 |
| 447 | *Verdigris silt loam* Labette Co., Kans. | 0–13 | Brown silt loam with slight grayish brown color when dry | 6.0 |
| | | 13–36 | Light-brown silty loam friable to about 20 inches, then approaches silty clay loam | 5.6 |
| 448 | *Verdigris silty clay loam* Marion Co., Kans. | 0–8 | Very dark brown heavy silty clay loam | 7.3 |
| | | 8–12 | Dark brown silty clay | 6.7 |
| | | 12–20 | Dark brown clay—medium friable | 6.5 |
| | | 20–40 | Light brown uniform silty clay to clay | 6.8 |
| | | 40–72 | Stratified layers very fine sandy clay to clay, brown to dark grayish brown | 7.1 |
| | | 72–82 | Brown to dark brown silty clay | 7.3 |
| | | 82–96 | Dark brown clay | 7.1 |
| | | 96–120 | Dark olive gray to olive-brown friable clay | 7.4 |

TABLE 29—*Continued*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 449 | *Lightning silt loam* Labette Co., Kans. | 0–15 | Light brown to grayish brown silt loam | 5.9 |
| | | 15–40 | Grayish brown mottled rusty brown silty clay loam | 5.2 |
| 450 | *Osage clay* Labette Co., Kans. | 0–24 | Very dark gray tough clay | 5.8 |
| | | 24–40 | Gray plastic clay slightly mottled with yellowish brown | 5.3 |
| 451 | *Osage silty clay loam* Labette Co., Kans. | 0–7 | Dark gray to dark brownish gray clay loam | 6.0 |
| | | 7–40 | Light brownish gray silty clay loam | 6.1 |
| 452 | *Lamoure silty clay loam* Colfax Co., Nebr. | 0–¾ | Almost black silty clay to clay loam | 7.9 |
| | | ¾–5 | Black silty clay loam | 8.1 |
| | | 5–15 | Almost black silty clay loam | 8.2 |
| | | 15–29 | Dark gray silty clay loam | 8.3 |
| | | 29–74 | Dark gray clay | 8.4 |
| | | 74–92 | Light gray very fine sand and clay | 8.2 |
| 454 | *Havre silty clay loam* Lower Yellowstone area, Mont. | 0–12 | Brown silty clay loam, calcareous | 8.1 |
| | | 12–32 | Light-brown very fine sand with thin horizons of silt, calcareous | 8.5 |
| | | 32–48 | Light-brown very fine sand, calcareous | 8.6 |
| 455 | Middle Yellowstone area, Mont. | 0–6 | Brown somewhat granular silty clay, calcareous | 8.0 |
| | | 6–27 | Light brown calcareous silt loam | 8.8 |
| | | 27–40 | Brown fine sandy loam, calcareous | 8.6 |
| 456 | *Harlem clay* Middle Yellowstone area, Mont. | 0–8 | Dark gray silty clay, calcareous | 8.8 |
| | | 8–26 | Olive gray clay, calcareous | 8.8 |
| | | 26–48 | Brown very fine sand, calcareous | 9.2 |
| 457 | Milk River Valley area, Mont. | 0–27 | Dark gray to black heavy compact clay contains white flecks of lime | 7.8 |
| | | 27–36 | Light grayish brown heavy clay loam streaked with light gray and rusty brown | 8.6 |
| | | 36–50 | Light brownish gray fine to very fine sandy loam, friable | 8.0 |
| 458 | *Bowdoin clay* Milk River Valley area, Mont. | 0–28 | Slate gray compact clay flecked with salt accumulations | 8.2 |
| | | 28–36 | Light brownish gray clay streaked with light gray, calcareous | 7.8 |
| | | 36–52 | Light brownish gray calcareous fine sandy loam, light gray and brown mottling | 7.9 |

TABLE 29—*Concluded*

| PROFILE NUMBER | LOCATION | DEPTH | DESCRIPTION OF HORIZON | pH |
|---|---|---|---|---|
| | | *inches* | | |
| 459 | Northern Plains, Mont. | 0–4 | Dull light grayish brown clay | 8.3 |
| | | 4–10 | Dull dark brown clay | 8.5 |
| | | 10–24 | Dull, somewhat lighter-brown, tough plastic clay, some small whitish salt spots | 7.8 |
| | | 24–40 | Dull, somewhat lighter brown tough plastic clay with more whitish salt spots than above | 7.9 |
| 464 | *Billings loam* Basin area, Wyo. | 0–4 | Pale reddish brown thinly laminated loam strongly calcareous, many fine roots | 8.6 |
| | | 4–10 | Slightly compact light yellowish brown loam strongly calcareous slightly prismatic structure | 8.7 |
| | | 10–15 | Similar but more friable than above, small amount of white lime accumulation | 9.0 |
| | | 15–40+ | Reddish brown alternating layers of fine sandy loam and loam strongly calcareous. Roots extend below bottom of profile | 8.3 |
| 465 | *Billings clay loam* Uinta River Valley area, Utah | 0–½ | Very light brownish gray gritty clay loam, calcareous | 8.7 |
| | | ½–3 | Light brownish gray gritty clay loam, calcareous | 8.7 |
| | | 3–15 | Very light brownish gray gritty clay loam, calcareous compact streaked with lime | 8.4 |
| | | 15–72 | Very light brownish gray gritty clay loam, streaked with lime, calcareous | 7.8 |
| 467 | *Billings clay* Arkansas Valley area, Colo. | 0–2½ | Brown granular clay | 8.1 |
| | | 2½–10 | Olive-brown clay | 7.9 |
| | | 10–30 | Olive-brown clay with white material | 8.4 |
| | | 30–60 | Dull brown clay with small gravel and sand | 7.4 |
| 468 | *Holtville silty clay* Palo Verde area, Calif. | 0–6 | Pale brown silty clay | 8.2 |
| | | 6–38 | Pale brown compact clay | 8.0 |
| | | 38–72 | Light brown, loose fine sand | 8.8 |
| 469 | *Holtville clay* Palo Verde area, Calif. | 0–2 | Very pale brown compact clay | 8.2 |
| | | 2–34 | Pale brown compact clay | 8.1 |
| | | 34–38 | Pale brown clay mottled with yellowish brown | 8.2 |
| | | 38–72 | Very light brown loose fine sand | 8.3 |
| 470 | *Holtville silt loam* Palo Verde area, Calif. | 0–6 | Pale brown mellow silt loam | 8.6 |
| | | 6–12 | Pale brown smooth silt loam mottled with brownish yellow | 8.4 |
| | | 12–24 | Pale brown friable silt loam | 8.5 |
| | | 24–72 | Very light brown fine sand | 8.8 |

from material carried down from the uplands of those regions (13). It occurs in eastern North and South Dakota, northwestern Iowa, central and eastern Nebraska, and western Minnesota. It is imperfectly drained and limy.

The Havre, Harlem, and Bowdoin soils occur in the chestnut soil region in Montana (8, 9, 11). The Havre series is the best drained of the three. The Bowdoin is somewhat similar to the Harlem but is more inclined to be an "alkali" soil.

The Billings soils are on recent alluvial fans and small streambottoms (14, 36, 38). The material is derived from the shales of the uplands. This series occurs in the sierozem and desert regions of Colorado, Utah, and Wyoming. It is sometimes an "alkali" soil.

The Holtville series is found on heavy alluvium in the red desert region in California (23).

In the alluvial soils there is a great variance in the pH values, which are those of the parent materials. Thus the Stendal, from material containing very little lime, is more or less acid, especially near the surface, whereas the Huntington, from limestone materials, is neutral to alkaline for the most part. The Verdigris, Lightning, and Osage series have similar reactions to the upland prairie soils from which they are derived (3, table 16). In like manner, the Lamoure, Havre, Harlem, Bowdoin, Billings, and Holtville show a strong tendency to have pH values similar to those of the upland soils from whence they came (2, tables 2, 3, 5, 7, 8, 9; 3, table 16). None of the alluvial soils in the pedocal regions have developed zones of lime accumulation.

## SUMMARY

The pH values of the lithosols and alluvial soils cover a wide range and seem to be most nearly related to the character of the parent material.

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# BOOKS

*Annual Review of Biochemistry.*   Volume 14.   Edited by JAMES MURRAY LUCK AND JAMES H. C. SMITH.   Annual Reviews, Inc., Stanford University, California.   1945.   Pp. 856.   Price, $5.

The subjects covered in this highly important volume of recent findings in biochemistry include oxidations, reductions, enzymes, the chemistry of carbohydrates, lipids, amino acids, proteins, nucleic acids, nucleoproteins, steroids, sulfur compounds, phosphorus compounds, triterpenes, hormones, bacteria and antibiotics, the metabolism of carbohydrates, fats, proteins, and minerals, and a variety of other topics, such as x-ray studies, vitamins, detoxication, malignant tissues, nitrogen fixation, and the mineral nutrition of plants.   The author index includes nearly 5,000 names, an extensive bibliography being appended to each of the 28 chapters in the book.   Any man engaged in research in biochemistry and related fields will find material of interest and value in this systematic review of the literature.

*Lantbruks-Högskolans Annalar.*   Volume 12.   Almqvist & Wiksells Botrycker AB, Uppsala, Sweden, 1944–5.   Pp. 267.

This current volume of the Annals of the Agricultural College of Sweden contains a number of papers of interest to soil scientists, dealing with such topics as cellulose decomposition, saline irrigation waters, respiration of wheat roots, acid-base condition in vegetation and humus, atmospheric salts, Ca/K ratios, vitamin C metabolism in potatoes, Edin's indicator method for digestibility of feeds, amylase, avitaminosis, base saturation in relation to Donnan systems, soil-colloid dispersion, and the microdetermination of boron.   Included also is a complete index to volumes 1 to 12.

*A Manual of the Aspergilli.*   By CHARLES THOM AND KENNETH B. RAPER.   The Williams & Wilkins Company, Baltimore, 1945.   Pp. 373, figs. 76.   Price, $7.

The purpose of this manual is to present to workers in this field the methods for identifying Aspergilli and to record all the forms found in the literature and their proper allocation.   The book is based upon comparative studies of thousands of strains of Aspergilli in pure culture over a period of 40 years.   Two distinct bibliographies are presented.   The first is a topical one covering such subjects as acid production, antibiotics, chemistry of mold tissue, enzyme production, fat production, pathogenicity, physiology, pigments, vitamins, and miscellaneous products, such as alcohol, chitin, and gums.   The second is alphabetical in accordance with the authors' names.   It is difficult to do justice to this highly important contribution to the literature in such a short review.   Suffice it to say that every person interested in this line of research will want a copy of the book in his personal library.

*The Measurement of Colour.* By W. D. WRIGHT. Jarrell-Ash Company, Boston, 1944. Pp. 223, figs. 65. Price $9.75.

This is a concise scientific presentation of the principles of color measurement and the methods by which it can best be accomplished. Visual and photoelectric instruments and the uses of color physics in technical processes are described. The several chapters deal with radiation in the visible spectrum, its emission, absorption, reflection, and reception by the eye, the trichromatic system of color measurement, the design and use of colorimeters, spectrophotometry applied to color measurement, the color atlas, and applications in agriculture and industry. The appendix deals with illuminants, the C.I.E. system of color specification, and condensed tables for color computation. All those concerned with this field of study will find this a very instructive and useful book.

*Proceedings of the Twenty-fifth Annual Convention of the Michigan Muck Farmers' Association.* Secretary-Treasurer, Paul M. Harmer, East Lansing, Michigan. Pp. 48.

This is a report of the meeting held at Michigan State College, East Lansing, Michigan, February 3 and 4, 1943. Of the papers presented at the convention, those on Russian dandelion, potatoes, sugar beets, head lettuce, celery, new varieties of vegetables, onions, and mint are of special interest.

*Scientific Societies in the United States.* By RALPH S. BATES. John Wiley and Sons, Inc., New York, 1945. Pp. 246. Price, $3.50.

The theme of this book is that of the history and influence of the scientific societies of the United States. The chapter headings are: Scientific Societies in the Eighteenth Century; National Growth, 1800–1865; the Triumph of Specialization; American Scientific Societies and World Science, 1919–1944; and the Increase and Diffusion of Knowledge. Credit for being "the first scientific society in the modern world" is given to the Academia Secretorium Naturae, established in Naples in 1560. The Boston Philosophical Society, promoted by Increase Mather in 1683, was the first to come into existence in the United States, but it soon expired. To the American Philosophical Society, proposed by Benjamin Franklin in 1743 and still in existence, goes the greater honor. The book contains a wealth of material of interest to members of the several scientific societies, not the least of which is the chapter dealing with the public benefits derived from the activities of these societies. The bibliography and index, covering 53 pages, will be found especially useful for reference purposes. Incidentally, the Soil Science Society of America is not listed in the book.

*Vegetable Production and Marketing.* By PAUL WORK. John Wiley and Sons Company, Inc., New York, 1945. Pp. 559, figs. 186. Price, $2.75.

This book is designed for classroom use in a general course in vegetable production. It contains 28 chapters dealing with such diverse topics as vegetable

farm management, marketing, roadside selling, equipment, seed, plants, soils, irrigation, insects, storage and exhibition of vegetables, and has special chapters on potatoes, sweet potatoes, tomatoes, sweet corn, root crops, peas and beans, vine crops, onions, cabbage, celery, lettuce, spinach, asparagus, and rhubarb. A great deal of practical knowledge is necessary in the writing of such a book, and this book shows plenty of evidence that the author knows his subject.

THE EDITORS.

# THE VALUE OF PRELIMING, PRIMARILY AS A MEANS OF IMPROVING THE ABSORPTION OF PHOSPHORUS BY PLANTS

B. E. BEATER

*Experiment Station of the South African Sugar Association, Mount Edgecombe, Natal*[1]

In many soils there appears to be a wasteful application of soluble phosphates, wasteful because the phosphates are more or less permanently fixed in the soil before they can be utilized fully by the plant. An obvious solution would be to try to condition the soil chemically so as to prevent the loss of such phosphates. The object of the work described in this paper was to determine to what degree lime can assist in the absorption of phosphates by plants. For this purpose, several representative soils of the sugar belt of Natal and Zululand were selected and were studied along lines suggested by earlier approaches to this problem.

## BEHAVIOR OF SOLUBLE PHOSPHATES IN SOIL

Attention has long been drawn to the fact that many, if not most, soils retain soluble phosphates in such a manner that they can be only partly removed by the common solvents. Extremely sandy soils retain only a minute quantity of the added element; very clayey soils, on the other hand, retain disproportionately large quantities. The problem is thus relegated largely, though not exclusively, to soils of heavier composition. Moreover, the quality of the clay is as important a factor in the retention of phosphate by the clay fraction as is the quantity. Thus Murphy (36, 37) found that kaolinitic clay had a greater adsorptive capacity than montmorillonitic clay. Coleman (11), however, found that oats and cotton did not differentiate between the two forms of clay.

Of the three elements primarily responsible for phosphate retention in the soil; namely, iron, aluminum, and calcium, only the first two will be considered at this stage. Romine and Metzger (45) found that low availability of phosphate was associated with low pH values. Raychaudhuri and Mukherjee (43) reported an increase in phosphorus fixation with an increase in HCl-soluble $R_2O_3$. Metzger (34) asserted that the total $R_2O_3$, $Fe_2O_3$, and $Al_2O_3$ of the soil showed, in each case, a highly significant correlation with phosphorus-fixing capacity. Various investigations have shown that it is the easily removable iron and aluminum oxides that are most responsible for phosphate retention. Thus Chandler (10) found that extraction of the free iron and aluminum oxides from the clays caused a reduction in the phosphorus-adsorptive capacity in almost every case. Metzer (33) also found that easily extractable iron and aluminum play an important part in phosphorus fixation.

The writer found (7) that clayey soils adsorbed soluble phosphates with extreme rapidity. In a recent method of his, the period of contact was reduced

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to one-half minute, when it was found in some cases that most of the soluble phosphate could be fixed. And, as has been mentioned, this fixation was not always directly proportional to the clay content alone. Allison *et al.* (4) have reported that a high colloidal or clay content, especially if iron and aluminum oxides are abundant, leads to marked phosphate fixation. It has also been amply demonstrated (8, 46, 53) that the movement of soluble phosphates in soil is very slight.

The role of organic matter is generally considered of minor importance in phosphate fixation. Bertramson and Stephenson (9) have pointed out that availability of organic phosphate is in part a biological phenomenon. The old soils have become biologically inactive, and the old resistant residue of humus no longer decomposes readily or liberates appreciable quantities of phosphorus. Allison *et al.* (4), in common with other investigators, have found that in most cases organic phosphates are converted fairly rapidly into inorganic phosphates. The phenomenon of fixation thus appears to be largely a function of the clay or colloidal properties of the soil, and as this may reach serious proportions, in certail soils, an alternative procedure would be to select crops which can utilize the difficultly available phosphates. Coleman (11) in this manner found that cotton and oats can utilize adsorbed phosphate very effectively from acid soils. But where an industry is given over to the extensive production of a single commodity, like the sugar industry of this country, such a program would not be feasible. The only obvious angle of approach would appear to be one in which the soil is so conditioned that the fixed phosphate can be rendered less unavailable. Though iron (and perhaps aluminum) phosphates may be a slow but certain supply of phosphate to numerous crops (19), the fact remains that soluble phosphates do not produce a response on many treated soils, and the continued addition of the fertilizer would become uneconomical. The order of stability of fixed phosphorus compounds in the soil varies significantly with the pH value, which suggests that a ready solution to the problem may lie in an alteration of the degree of base saturation of the soil. Naftel (38) has reported that the formation of calcium phosphates in aqueous solutions is as follows: monobasic, pH 3.0 to 5.0; dibasic, pH 5.0 to 6.4; and tribasic, above pH 6.4. He has also reported that the presence of excess Ca in an alkaline medium forms a more basic salt than the tribasic phosphate, probably hydroxy-apatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$.

## EFFECT OF LIMING ON SOIL PHOSPHATES

That adjustment of the soil reaction must not be considered in itself a solution to the problem has been pointed out by Albrecht, Schroeder, and Smith (2, 3). Calcium in the soil is, in their view, a factor which modifies the physiology of the plant. The plant, behaving like an ampholyte, adsorbs phosphorus more readily in one physiological state than in another. This outlook, which was discussed earlier by Davidson (13), emphasizes the possibility that the phenomenon may involve something more than the older concept of acidity. However this may be, there is overwhelming evidence of the fact that the liming of soils

in conjunction with phosphate fertilization is highly beneficial. MacIntyre and Hatcher (31) have suggested that the ideal would be to effect complete neutralization of the acidic and phosphate-fixing portions of the soil by a thoroughly disseminated liming material during an adequate interval before incorporation of the acidic superphosphate. The conditions that favor persistence of dicalcium phosphate are the ones that should give the best returns from superphosphate additions to limed soils, and such conditions can be found only in a moderately limed soil. Tricalcium phosphate contains considerably less citrate-soluble $P_2O_5$ than does dicalcium phosphate, and the formation of the tricalcium compound, together with a possible precipitation of calcium fluorphosphate, might account for the occasional repressive effect of heavy liming upon response from superphosphate. MacIntyre and Hatcher have pointed out that the formation of tricalcium phosphate in itself would not be sufficient indictment of overliming, but unfortunately the undesirable fluoride content of the phosphatic fertilizer also militates against the practice.

There is evidence to show that tricalcium phosphate forms somewhat slowly. MacIntyre and Hatcher have concluded, from a study of the effects of preliming, that a preparatory liming would assure substantial conversion of an incorporated superphosphate to the readily available form of dicalcium phosphate and promote the continuance of that phosphate for a period sufficient for the initial crop to register an enhancement in $PO_4$ uptake. Overliming is, on the whole, not too deleterious, then, as the formation of tricalcium phosphate is distinctly more desirable than the formation of either the iron or aluminum compounds (16). In this connection Moser (35) found that fixed phosphate in the tricalcium form gave a better growth response in soils than did the predominating aluminum form. The time required for complete revision of soluble phosphatic fertilizer to tricalcium phosphate on the addition of lime is relatively long, perhaps 2 or 3 years (21).

Liming does not always have the effect of producing responses to phosphate dressings in acid soils. Thus Perkins et al. (42) found that small amounts of lime added with a phosphate dressing resulted in decreased plant growth and decreased phosphorus adsorption; larger applications, however, reversed this behavior. McGeorge (28) also found that calcium hydroxide and calcium carbonate reduced the availability and absorption of phosphate. Karraker et al. (23) found that liming materially decreased the availability of rock phosphate and colloidal phosphate, and slightly decreased the availability of tricalcium phosphate in greenhouse tests. Vanderford (52) pointed out that the phosphorus content of soybeans and sweet clover and the total amount removed from the soil decreased with increasing increments of calcium carbonate, but the total amount of phosphorus removed by lespedeza increased with each addition of calcium carbonate. Naftel (38) showed that increased liming increased the calcium in the plant, but phosphorus absorption varied with soil type.

Further evidence on the value of preliming is given by numerous other investigators. Thus, Stewart (48) maintained that liming acid plots greatly increased the effectiveness of phosphates. Kirsanov and Kirsanova (24) asserted

that lime increased the effects of both superphosphate and apatite.    Thomas and Mack (49), studying foliar diagnosis, found that the $P_2O_5$ content of the third leaf from the base of the stalk of maize plants increased by more than 70 per cent as a result of liming.    Naftel (38, 39) also showed that lime added to the soil more than doubled the solubility of residual phosphorus.    The work of Cook (12) revealed that the addition of lime to soils caused significant increases in the amounts of readily available soil phosphates.    This was demonstrated also by Dunn (15) for more acid soils.    Dunn suggested that the increases in calcium saturation of the soil colloidal complex may have made phosphorus, and potassium, more available to plants.    Roberts *et al.* (44) have shown that applications of limestone significantly increased the effectiveness of phosphates on hay.    Ayres (5) asserted that superphosphate and reverted phosphates on limed soil resulted in larger yields than on unlimed soil.    Albrecht and Klemme (1) succeeded in mobilizing the phosphorus more effectively into the crop by the joint use of phosphate and limestone.    Longnecker and Sprague (26) found that lime in the form of hydroxide became caked and dissolved more slowly than did limestone.    Willard and Smith (55) also reported that the hydroxide was slightly less effective, though only in the subsoil.    Parker and Tidmore (41) found that liming increased the phosphorus content of the soil solution and of the extracts from soils receiving acid phosphate or basic slag but had little or no effect on rock phosphate.    In their experience, liming had a very decided depressing effect on the solubility of phosphorus in steamed bone meal.    Ghani and Aleem (17) concluded that the rise in the pH of the soil is the principal factor in determining the degree of increased availability of soil phosphorus due to liming.    The change in the soil reaction toward neutrality favors greater microbiological activities, which in turn effect greater breakdown of organic phosphorus compounds.    These workers went so far as to say that increased availability as a result of liming is due solely to breakdown of organic phosphorus.

From the foregoing summary it would appear that preliming is advantageous. The whole question was aptly summarized by Gilligan (18) when he suggested that from a practical standpoint it is advisable to maintain the soils, at any rate those which he investigated, at a calcium level sufficiently high to avoid the formation of insoluble iron and aluminum phosphates, yet somewhat below complete saturation, where insoluble calcium phosphate is precipitated.    Krügel *et al.* (25) voiced a similar sentiment when they said that mere application of phosphoric acid to the soils they studied was insufficient, since crops were considerably increased by applications of suitable quantities of lime in addition to dressings of phosphoric acid.    In their view, liming forms the basis of fertilization in order to bring about a satisfactory calcareous condition of the soil. This improved status of the soil, brought about by liming, may be due to an improved physical condition.    It may also be due to the fact that lime itself, as opposed to the release of phosphates, can bring about increased growth. This point has been demonstrated by Tiedjens (50), who found that lime was a necessary plant food, and that increased production resulted from applications of lime alone.    Dunn (15) also found this to be the case.    A further benefit

resulting from the application of lime may be the stimulation of nitrate productivity (54), though as Searle pointed out (47, p. 537), the addition of lime to a soil does not necessarily increase the amount of nitrate present.

Lastly, in connection with the economic value of liming, it is well to note that loss of lime from the soil, other than through the medium of the plant, is not unduly heavy. Doak (14) showed that calcium either as the carbonate or as exchangeable lime did not leach below 10 inches over a period of 4 to 5 years.

TABLE 1

*Correlation between foliar symptoms of the tomato and availability of soil phosphate*

| SOIL NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Soil texture............. | Loamy fine sand | Clay loam | Coarse sand | Coarse sandy loam | Loamy sand | Sandy loam | Clayey silt loam |
| Available $P_2O_5$ per acre 7 inches* ... *pounds*... | 52 | 7 | 18 | 20 | 12 | 65 | 10 |
| Symbol for $P_2O_5$ availability† .............. | M | VL | M-L | L | VL | H | VL |
| $P_2O_5$ fixed per acre 7 inches‡ ... *pounds*.... | 45 | 60 | 45 | 78 | 65 | 50 | 92 |
| Symbol for P fixation†... | L | M | L | H | M | L | H |
| Difference in size of plants over controls... | Moderate | Pronounced | Moderate | Moderate | Pronounced | None | Pronounced |
| Foliar symptoms of P deficiency.............. | Absent | Pronounced | Absent | Very pronounced | Moderately pronounced | Absent | Pronounced |

\* Beater, B. E. 1941 Estimation of the availability of phosphoric acid, potash, and nitrogen in soils by a new rapid technique. *Proc. So. African Sugar Tech. Assoc.* 1941: 113–120.

† M = medium, L = low, VL = very low, H = high.

‡ Unpublished method.

Truog (51) reported the loss of lime as calcium oxide from soils, over and above that returned in the form of manures and crop residues, to be from 50 to 250 pounds per acre. The loss of lime, however, varies greatly with soil and climatic conditions. Generally it appears to be regarded as not a very serious problem in agriculture.

### THE TOMATO AS AN INDICATOR OF PHOSPHATE DEFICIENCY

Before the main experimental work outlined in this paper was begun, a suitable indicator plant for detecting phosphate deficiency in soils had to be found in order to establish the phosphate requirements of some of the representative soil series of the sugar belt. The tomato, which has been widely used (6, 20, 22, 27, 29, 32, 37, 40) as an indicator plant, was selected because of its particular sen-

sitivity to phosphate deficiency. This sensitivity is marked by a characteristic purpling of the undersides of the leaf in phosphate-deficient soils.

Seven soils from various districts of Natal and Zululand were selected for study, as follows:

Soil 1. Derived from Ecca shale. Moderately productive but with a tendency to cement during dry spells.

Soil 2. Derived from dolerite. A rich soil but low in available phosphates.

Soil 3. Of wind-blown origin, extremely poor and sandy.

Soil 4. Derived from Table Mountain sandstone. Particularly acid and only moderately productive.
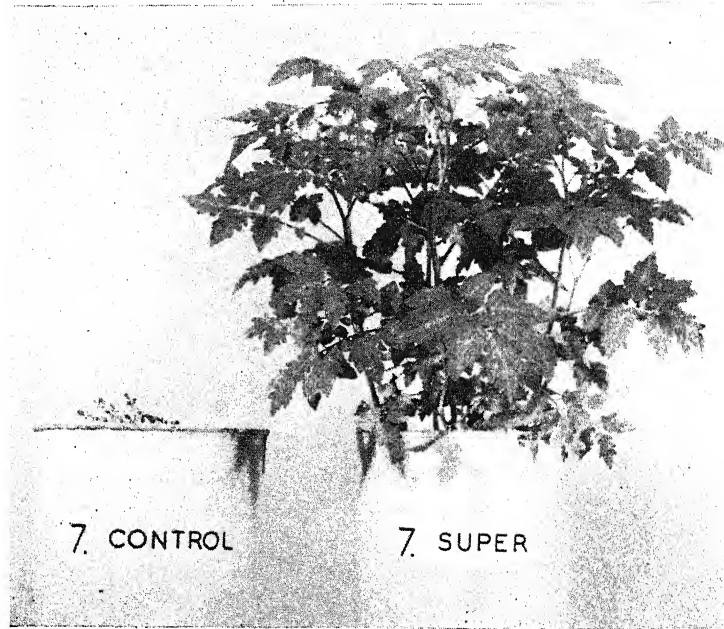


FIG. 1. EFFECT OF SUPERPHOSPHATE ON 10-WEEK-OLD TOMATO PLANTS IN SOIL NATURALLY VERY DEFICIENT IN AVAILABLE PHOSPHATES

Soil 5. Similar in most respects to soil 1.

Soil 6. Derived from granite. Highly productive.

Soil 7. Derived from dolerite. Similar in many respects to soil 2 except that it lies at a higher altitude where it has undergone more leaching, resulting in a rather acid state. This soil is extremely deficient in available phosphate.

All these soils were placed in pots, 15 pounds to a pot, and superphosphate was intimately mixed in at the rate of 500 pounds per acre. Tomatoes of the variety Stone were planted in duplicate pots, and the soil was kept moderately moist. When the plants were 5 weeks old, observations were made on foliar symptoms and growth. Table 1 summarizes these observations and gives other relevant data.

When the plants were 10 weeks old the response was almost in inverse order of the quantity of available phosphate in the soil as determined by chemical

tests. Where the soil was highly deficient in available phosphate, *e.g.*, soil 7, the addition of superphosphate resulted in a most spectacular response by the tomato (fig. 1). It would seem, then, that the tomato offers much promise in determining the phosphate requirements of soils. The results of these experiments also showed a good correlation between the behavior of the plants and the author's rapid chemical tests for phosphates.
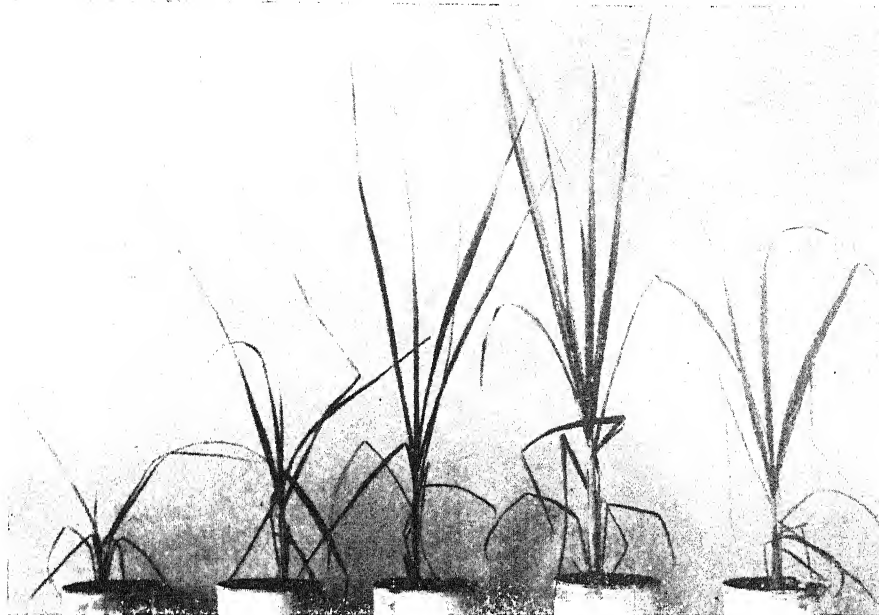


FIG. 2. EFFECT OF CALCIUM CARBONATE ON THE GROWTH OF SUGAR CANE IN A HIGHLY ACID SOIL

Left to right: control, 1 ton CaCO₃ per acre, 2 tons CaCO₃ per acre, 3 tons CaCO₃ per acre, 4 tons CaCO₃ per acre.

### EFFECT OF LIMING ON SOIL REACTION

The effect of liming on the soil reaction and fertility of the seven selected soils was next studied. Table 2 shows the chemical and physical composition of these soils. The chemical composition was measured by refluxing the soil for 1 hour with HCl of 1.115 sp. gr., and the physical composition by a modification of the pipette method.

The liming treatments consisted in applying weighed quantities of precipitated calcium carbonate to each pot containing 15 pounds of soil. The amounts applied were calculated to equal 1, 2, 3, and 4 tons of CaCO₃ per acre 2,000,000 pounds soil. The calcium carbonate was intimately mixed with the sieved soil, and samples were taken immediately for pH determinations by the glass electrode. Because of the formation of $CO_2$, the technique followed in obtaining pH values in this experiment was to mix 2.5 gm. soil with 25 ml. distilled water, shake for 3 minutes, and then allow the suspension to stand 24 hours. Following this,

air was drawn through the suspension for 15 minutes before electrical measurements were taken. The soil in the pots was kept reasonably moist, at about 20 per cent of the water-holding capacity, and pH values were retaken after 4 weeks, 9 weeks, 5 months, and 13 months.

After 9 weeks the soil was remixed, and the pots were planted with maize, which was harvested after $2\frac{1}{2}$ months, when the liming experiment had proceeded 5 months. The soil was again remixed, and the pots were planted with sugar cane sets. These plants were harvested in 8 months, making the duration of the experiment at this point 13 months.

The pH determinations are shown in table 3.

TABLE 2

*Chemical and physical composition of seven representative soils of the sugar belt*
Results expressed in percentages of oven-dry soil

| SOIL NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| *Chemical composition* | | | | | | | |
| Insoluble in HCl (1.115 sp. gr.).... | 92.00 | 66.03 | 96.43 | 76.02 | 80.35 | 82.77 | 54.68 |
| Soluble silica ($SiO_2$)............... | 0.19 | 0.16 | 0.53 | 0.16 | 0.11 | 0.20 | 0.31 |
| Calcium oxide (CaO).............. | 0.15 | 0.51 | 0.10 | 0.14 | 0.24 | 0.34 | 0.29 |
| Magnesium oxide (MgO)........... | 0.32 | 0.95 | 0.15 | 0.29 | 0.69 | 1.33 | 0.69 |
| Potash ($K_2O$)..................... | 0.03 | 0.13 | 0.02 | 0.04 | 0.12 | 0.36 | 0.08 |
| Phosphoric oxide ($P_2O_5$)......... | 0.02 | 0.07 | 0.01 | 0.09 | 0.06 | 0.06 | 0.12 |
| Iron oxide ($Fe_2O_3$)............... | 3.25 | 11.66 | 1.47 | 5.73 | 9.97 | 3.22 | 11.86 |
| Alumina ($Al_2O_3$).................. | 1.24 | 9.19 | 0.29 | 7.78 | 3.57 | 6.16 | 15.49 |
| Titanium oxide ($TiO_2$)............ | 0.28 | 0.63 | 0.24 | 0.12 | 0.14 | 0.09 | 0.21 |
| Manganese oxide (MnO).......... | 0.01 | 0.07 | 0.03 | 0.01 | 0.03 | 0.03 | 0.14 |
| Loss on ignition.................. | 2.76 | 11.53 | 1.06 | 9.81 | 4.94 | 6.63 | 16.28 |
| Organic matter................... | 2.10 | 5.20 | 0.50 | 4.40 | 2.40 | 4.00 | 7.40 |
| Moisture at 105° C............... | 1.43 | 10.43 | 0.40 | 3.95 | 3.26 | 2.96 | 10.61 |
| *Physical composition* | | | | | | | |
| Coarse sand (2–0.2 mm.).......... | 24.18 | 6.66 | 71.27 | 41.16 | 31.09 | 38.08 | 17.07 |
| Fine sand (0.2–0.02 mm.)......... | 57.96 | 34.51 | 23.67 | 25.67 | 36.05 | 29.01 | 17.93 |
| Silt (0.02–0.002 mm.)............. | 10.20 | 14.01 | 2.53 | 7.65 | 17.69 | 10.13 | 26.07 |
| Clay (<0.002 mm.).............. | 7.66 | 44.82 | 2.53 | 25.52 | 15.17 | 22.78 | 38.93 |

The effect of lime on the pH value appeared to be dictated by the physical composition of the soil and the amount of native calcium already absorbed. With the exception of soil 4, the pH value resulting from the immediate favorable interaction of lime with the soil was no further affected, one way or the other, over the 13-month period. In soil 4, however, the pH values decreased steadily with all treatments. In several cases the control pH values altered appreciably, though pH measurements checked against the original bottled soil showed no change. Further experiments with these soils showed that their lime requirements varied greatly. For example, whereas $\frac{1}{4}$ ton $CaCO_3$ per acre was sufficient to bring soil 3 to a pH value of 7.5, no less than 6 tons $CaCO_3$ per acre was re-

quired to bring soil 7 to an equivalent pH value. It is interesting to note that soil 2 could be brought to pH 7.5 with just over 1 ton $CaCO_3$ per acre, yet this

TABLE 3

*Effect of calcium carbonate on soil reaction*

| SOIL NUMBER | TREATMENT* | INITIAL pH VALUE | pH VALUE IMMEDI- ATELY ON APPLICATION | pH VALUE AFTER STANDING | | | |
|---|---|---|---|---|---|---|---|
| | | | | 4 weeks | 9 weeks | 5 months | 13 months |
| 1 | Control | 6.4 | 6.4 | 6.4 | 6.3 | 6.4 | 6.7 |
| | 1 ton $CaCO_3$ | 6.4 | 7.8 | 7.2 | 7.1 | 7.2 | 7.4 |
| | 2 tons $CaCO_3$ | 6.4 | 8.0 | 7.9 | 7.8 | 7.9 | 7.8 |
| | 3 tons $CaCO_3$ | 6.4 | 8.0 | 8.1 | 8.2 | 8.1 | 8.1 |
| | 4 tons $CaCO_3$ | 6.4 | ... | 8.3 | 8.3 | 8.1 | 8.2 |
| 2 | Control | 5.9 | 5.9 | 5.8 | 5.8 | 6.1 | 6.4 |
| | 1 ton $CaCO_3$ | 5.9 | 7.4 | 6.9 | 6.3 | 6.4 | 6.7 |
| | 2 tons $CaCO_3$ | 5.9 | 7.7 | 6.8 | 6.9 | 6.9 | 6.9 |
| | 3 tons $CaCO_3$ | 5.9 | 7.8 | 7.1 | 7.0 | 7.1 | 7.1 |
| | 4 tons $CaCO_2$ | 5.9 | 7.8 | 7.5 | 7.3 | 7.3 | 7.4 |
| 3 | Control | 5.2 | 5.2 | 6.0 | 5.6 | 6.0 | 7.4 |
| | 1 ton $CaCO_3$ | 5.2 | 7.9 | 7.6 | 7.2 | 7.4 | 7.9 |
| | 2 tons $CaCO_3$ | 5.2 | 7.9 | 8.0 | 8.0 | 8.0 | 8.6 |
| | 3 tons $CaCO_3$ | 5.2 | 7.9 | 8.2 | 8.2 | 8.3 | 8.7 |
| | 4 tons $CaCO_3$ | 5.2 | ... | 8.3 | 8.2 | 8.4 | 8.9 |
| 4 | Control | 4.7 | 4.7 | 5.0 | 5.1 | 5.2 | 5.2 |
| | 1 ton $CaCO_3$ | 4.7 | 5.7 | 5.6 | 5.6 | 5.1 | 5.2 |
| | 2 tons $CaCO_3$ | 4.7 | 6.7 | 5.9 | 5.8 | 5.7 | 5.5 |
| | 3 tons $CaCO_3$ | 4.7 | 7.2 | 6.3 | 6.0 | 5.8 | 5.7 |
| | 4 tons $CaCO_3$ | 4.7 | 7.3 | 6.6 | 6.4 | 5.9 | 5.9 |
| 5 | Control | 6.4 | 6.4 | 6.5 | 6.3 | 6.6 | 6.9 |
| | 1 ton $CaCO_3$ | 6.4 | 7.8 | 7.2 | 7.1 | 7.2 | 7.3 |
| | 2 tons $CaCO_3$ | 6.4 | 7.8 | 7.8 | 7.5 | 7.6 | 7.8 |
| | 3 tons $CaCO_3$ | 6.4 | 7.9 | 8.2 | 8.2 | 8.1 | 8.2 |
| | 4 tons $CaCO_3$ | 6.4 | 7.8 | 8.4 | 8.3 | 8.3 | 8.4 |
| 6 | Control | 5.3 | 5.3 | 5.6 | 5.4 | 5.9 | 6.2 |
| | 1 ton $CaCO_3$ | 5.3 | 6.8 | 6.3 | 5.5 | 6.0 | 6.4 |
| | 2 tons $CaCO_3$ | 5.3 | 7.3 | 6.7 | 6.3 | 6.6 | 6.7 |
| | 3 tons $CaCO_3$ | 5.3 | 7.6 | 7.2 | 6.9 | 7.0 | 7.2 |
| | 4 tons $CaCO_3$ | 5.3 | 7.7 | 7.7 | 7.1 | 7.2 | 7.3 |
| 7 | Control | 5.2 | 5.2 | 5.2 | 5.3 | 5.7 | 5.8 |
| | 1 ton $CaCO_3$ | 5.2 | 5.9 | 5.7 | 5.5 | 5.9 | 6.0 |
| | 2 tons $CaCO_2$ | 5.2 | 6.2 | 6.0 | 5.8 | 6.1 | 6.1 |
| | 3 tons $CaCO_3$ | 5.2 | 6.7 | 6.2 | 6.0 | 6.3 | 6.3 |
| | 4 tons $CaCO_3$ | 5.2 | 7.0 | 6.4 | 6.2 | 6.4 | 6.4 |

* All $CaCO_2$ treatments on an acre basis.

soil contains only a slightly smaller silt and clay fraction than does soil 7. A glance at the chemical composition shows that soil 2 is remarkably well stocked

## TABLE 4

*Effect of preliming on nitrogen, phosphorus, and calcium uptake of maize*
Results expressed on oven-dry material

| SOIL NUMBER | TREATMENT[a] | pH VALUE OF SOIL AT PLANTING | TOTAL NITROGEN (N) | PHOSPHORIC OXIDE ($P_2O_5$) | CALCIUM OXIDE (CaO) |
|---|---|---|---|---|---|
| | | | *per cent* | *per cent* | *per cent* |
| 1 | Control | 6.3 | 1.92 | 0.70 | 1.05 |
| | 1 ton $CaCO_3$ | 7.1 | 2.80 | 1.06 | 2.50 |
| | 2 tons $CaCO_3$ | 7.8 | 3.30 | 0.54 | 1.88 |
| | 3 tons $CaCO_3$ | 8.2 | 2.82 | 0.67 | . . . . |
| | 4 tons $CaCO_3$ | 8.3 | 3.10 | 0.88 | . . . . |
| | Av. of $CaCO_3$ treatments | | 3.01 | 0.79 | 2.19 |
| 2 | Control | 5.8 | 2.07 | 0.43 | 1.10 |
| | 1 ton $CaCO_3$ | 6.3 | 2.05 | 0.44 | 1.25 |
| | 2 tons $CaCO_3$ | 6.9 | 1.83 | 0.36 | 1.11 |
| | 3 tons $CaCO_3$ | 7.0 | 2.04 | 0.40 | 1.04 |
| | 4 tons $CaCO_3$ | 7.3 | 2.15 | 0.41 | 1.36 |
| | Av. of $CaCO_3$ treatments | | 2.02 | 0.40 | 1.19 |
| 3 | Control | 5.6 | 2.03 | 0.36 | 0.87 |
| | 1 ton $CaCO_3$ | 7.2 | 1.60 | 0.51 | 1.26 |
| | 2 tons $CaCO_3$ | 8.0 | 1.76 | 0.47 | 1.78 |
| | 3 tons $CaCO_3$ | 8.2 | 1.76 | 0.36 | 2.22 |
| | 4 tons $CaCO_3$ | 8.2 | 1.99 | 0.54 | 1.55 |
| | Av. of $CaCO_3$ treatments | | 1.78 | 0.47 | 1.70 |
| 4 | Control | 5.1 | Died soon after germination. | | |
| | 1 ton $CaCO_3$ | 5.6 | Survived longer, but also died. | | |
| | 2 tons $CaCO_3$ | 5.8 | Survived poorly. | | |
| | 3 tons $CaCO_3$ | 6.0 | Survived poorly. | | |
| | 4 tons $CaCO_3$ | 6.4 | Survived poorly. | | |
| 5 | Control | 6.3 | 0.96 | 0.42 | 0.60 |
| | 1 ton $CaCO_3$ | 7.1 | 1.65 | 0.53 | 0.56 |
| | 2 tons $CaCO_3$ | 7.5 | 2.59 | 0.57 | 1.32 |
| | 3 tons $CaCO_3$ | 8.2 | 2.39 | 0.85 | 1.51 |
| | 4 tons $CaCO_3$ | 8.2 | 1.66 | 0.61 | 1.37 |
| | Av. of $CaCO_3$ treatments | | 2.07 | 0.64 | 1.19 |
| 6 | Control | 5.4 | 1.82 | 0.54 | 1.08 |
| | 1 ton $CaCO_3$ | 5.5 | 2.43 | 0.61 | 1.05 |
| | 2 tons $CaCO_3$ | 6.3 | 2.47 | 0.77 | 1.10 |
| | 3 tons $CaCO_3$ | 6.9 | 2.66 | 0.52 | 1.32 |
| | 4 tons $CaCO_3$ | 7.1 | 2.50 | 0.69 | 1.28 |
| | Av. of $CaCO_3$ treatments | | 2.52 | 0.65 | 1.19 |

TABLE 4—*Continued*

| SOIL NUMBER | TREATMENT* | pH VALUE OF SOIL AT PLANTING | TOTAL NITROGEN (N) | PHOSPHORIC OXIDE (P₂O₅) | CACLIUM OXIDE (CaO) |
|---|---|---|---|---|---|
| | | | *per cent* | *per cent* | *per cent* |
| 7 | Control | 5.3 | 1.58 | 0.42 | 0.68 |
| | 1 ton CaCO₃ | 5.5 | 1.87 | 0.41 | 0.75 |
| | 2 tons CaCO₃ | 5.8 | 2.15 | 0.49 | 0.85 |
| | 3 tons CaCO₃ | 6.0 | 2.08 | 0.56 | 1.18 |
| | 4 tons CaCO₃ | 6.2 | 2.18 | 0.48 | 0.79 |
| | Av. of CaCO₃ treatments | | 2.07 | 0.49 | 0.89 |

\* All CaCO₃ treatments on an acre basis.

with native lime. These results demonstrate that the physical composition and native (replaceable) lime are the important factors in any liming policy.

### EFFECT OF PRELIMING ON GROWTH AND COMPOSITION OF THE PLANT

The effect of preliming on the growth and composition of maize and of sugar cane in the pots of soil was next investigated. In this paper, the accent is chiefly on the uptake of phosphorus as influenced by preliming. At the same time, since lime is believed to favor the formation of available nitrogen in the soil, nitrogen uptake also was studied. The absorption of calcium itself was examined, though calcium is regarded here primarily as a means of chemically conditioning the soil and thus stimulating chemical and biological activity. In one soil (soil 4), neither maize nor sugar cane grew successfully without added lime. Here lime produced a marked response up to 3 tons per acre and then gradually fell off at 4 tons (see figure 2). Nevertheless, lime itself is not here recorded as deficient (see table 2) but rather is too low to condition the soil chemically.

Table 4 gives the results of analyses of 3-month-old maize plants (excluding roots). The data show that calcium applications stimulated the uptake of nitrogen, phosphorus, and calcium, but not in proportion to the amount added to the soil. The uptake of calcium, however, showed a tendency to increase with increased calcium applications up to 3 tons per acre. At 4 tons per acre, less calcium tended to be absorbed than at 3 tons.

After the maize plants were taken for analysis, the soils in the pots were again mixed and were planted with sugar cane of the variety Co. 281. These plants were allowed to grow 8 months and were then cut and weighed. The oven-dry powdered material (excluding roots) was again analyzed for nitrogen, phosphoric oxide, and calcium. The percentage composition of this material is given in table 5.

As in the case of maize, there was a general increase in the three elements as a result of preliming. The one marked exception was nitrogen in soil 4. This can be explained by the fact that the control plant carried less stalk, and

## TABLE 5

*Effect of preliming on nitrogen, phosphorus, and calcium uptake of sugar cane*
Results expressed on oven-dry material

| SOIL NUMBER | TREATMENT* | pH VALUE OF SOIL AT PLANTING | TOTAL NITROGEN (N) | PHOSPHORIC OXIDE (P₂O₅) | CALCIUM OXIDE (CaO) |
|---|---|---|---|---|---|
| | | | *per cent* | *per cent* | *per cent* |
| 1 | Control | 6.4 | 0.35 | 0.17 | 0.84 |
| | 1 ton CaCO₃ | 7.2 | 0.50 | 0.18 | 0.88 |
| | 2 tons CaCO₃ | 7.9 | 0.56 | 0.18 | 1.01 |
| | 3 tons CaCO₃ | 8.1 | 0.63 | 0.19 | 1.12 |
| | 4 tons CaCO₃ | 8.1 | 0.63 | 0.17 | 0.76 |
| | Av. of CaCO₃ treatments | | 0.58 | 0.18 | 0.94 |
| 2 | Control | 6.1 | 0.36 | 0.10 | 0.79 |
| | 1 ton CaCO₃ | 6.4 | 0.44 | 0.14 | 0.91 |
| | 2 tons CaCO₃ | 6.9 | 0.39 | 0.12 | 0.71 |
| | 3 tons CaCO₃ | 7.1 | 0.36 | 0.12 | 0.80 |
| | 4 tons CaCO₃ | 7.3 | 0.41 | 0.17 | 1.11 |
| | Av. of CaCO₃ treatments | | 0.40 | 0.14 | 0.88 |
| 3 | Control | 6.0 | 0.39 | 0.16 | 0.71 |
| | 1 ton CaCO₃ | 7.4 | 0.40 | 0.18 | 1.74 |
| | 2 tons CaCO₃ | 8.0 | 0.46 | 0.24 | 1.86 |
| | 3 tons CaCO₃ | 8.3 | 0.47 | 0.13 | 1.60 |
| | 4 tons CaCO₃ | 8.4 | 0.38 | 0.20 | 2.19 |
| | Av. of CaCO₃ treatments | | 0.43 | 0.19 | 1.85 |
| 4 | Control | 5.2 | 1.95 | 0.15 | 0.96 |
| | 1 ton CaCO₃ | 5.1 | 2.02 | 0.14 | 1.30 |
| | 2 tons CaCO₃ | 5.7 | 1.55 | 0.14 | 1.05 |
| | 3 tons CaCO₃ | 5.8 | 1.31 | 0.14 | 1.11 |
| | 4 tons CaCO₃ | 5.9 | 1.68 | 0.15 | 1.29 |
| | Av. of CaCO₃ treatments | | 1.64 | 0.14 | 1.19 |
| 5 | Control | 6.6 | 0.40 | 0.15 | 0.72 |
| | 1 ton CaCO₃ | 7.2 | 0.42 | 0.23 | 1.00 |
| | 2 tons CaCO₃ | 7.6 | 0.42 | 0.26 | 1.11 |
| | 3 tons CaCO₃ | 8.1 | 0.46 | 0.21 | 0.77 |
| | 4 tons CaCO₃ | 8.3 | 0.77 | 0.29 | 1.61 |
| | Av. of CaCO₃ treatments | | 0.52 | 0.25 | 1.12 |
| 6 | Control | 5.9 | 0.36 | 0.12 | 0.43 |
| | 1 ton CaCO₃ | 6.0 | 0.45 | 0.19 | 0.33 |
| | 2 tons CaCO₃ | 6.6 | 0.38 | 0.20 | 0.45 |
| | 3 tons CaCO₃ | 7.0 | 0.45 | 0.12 | 0.58 |
| | 4 tons CaCO₃ | 7.2 | 0.83 | 0.18 | 0.66 |
| | Av. of CaCO₃ treatments | | 0.53 | 0.17 | 0.50 |

TABLE 5—*Continued*

| SOIL NUMBER | TREATMENT* | pH VALUE OF SOIL AT PLANTING | TOTAL NITROGEN (N) | PHOSPHORIC OXIDE ($P_2O_5$) | CALCIUM OXIDE (CaO) |
|---|---|---|---|---|---|
| | | | *per cent* | *per cent* | *per cent* |
| 7 | Control | 5.7 | 0.37 | 0.12 | 0.59 |
| | 1 ton $CaCO_3$ | 5.9 | 0.42 | 0.14 | 0.60 |
| | 2 tons $CaCO_3$ | 6.1 | 0.34 | 0.13 | 0.63 |
| | 3 tons $CaCO_3$ | 6.3 | 0.39 | 0.18 | 0.63 |
| | 4 tons $CaCO_3$ | 6.4 | 0.45 | 0.12 | 0.72 |
| | Av. of $CaCO_3$ treatments | | 0.40 | 0.14 | 0.65 |

* All $CaCO_3$ treatments on an acre basis.

the concentration of elements in leaves is always higher than in stalks. A factor such as this would assert itself in any experiment where the whole plant, without regard to size, is analyzed. The method of Thomas and Mack (49) in selecting a single leaf would perhaps be more suitable in a study of this kind.

In summarizing tables 4 and 5, involving some 200 analyses of dry plant material, it may be said that preliming has generally resulted in a 20 per cent increase in the uptake of phosphorus by the plant and has appreciably enhanced the uptake of nitrogen and calcium.

In all the soils used, rapid tests were periodically made, but with the exception of soil 1, no increase in available phosphorus was detected as a result of liming. It is apparent from the observations in this paper that even though extraction with a solvent (in this case 0.5 N $H_2SO_4$ buffered with very little sodium borate) showed no increase in available soil phosphorus, this nutrient was nevertheless being converted, probably into tricalcium phosphate, which was found to be very readily available, for example, to tomato plants.

The amount converted from the insoluble iron compound would be formed slowly and taken up at once by the plant. For this reason, rapid soil tests do not always indicate the chemical changes resulting from an experiment of this nature. Were plants not grown in the limed soils, an increase in available phosphate would perhaps have been detected as a result of liming. A broad review of the literature indicates that the beneficial effects of lime in releasing highly insoluble soil phosphate are beyond dispute. In the experiments described in this paper, all the soils examined showed an unmistakable tendency to liberate phosphate for the plant, even at reactions as extremely alkaline as pH 8.4. Results such as these suggest that, as a chemical corrective for plant growth, lime might well be given a more prominent place in agriculture.

### SUMMARY

In experiments on seven representative soils of the sugar belt of Natal and Zululand, the tomato was found to be a satisfactory indicator plant for phosphate deficiency.

The effect of calcium carbonate (1 to 4 tons per acre) on the reaction of the seven soils was traced over a 13-month period. The effect of lime on the pH

value appeared to depend on the physical composition of the soil and the native calcium already absorbed.

Maize plants, followed by sugar cane plants, were grown on the soils pre-limed to varying pH values, and the dry plant material was later analyzed for phosphates, nitrogen, and calcium. Preliming generally resulted in a 20 per cent increase in the concentration of phosphates in the dry substance, as well as an appreciable increase in the concentration of nitrogen and calcium.

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# WATER INFILTRATION AND RELATED SOIL PROPERTIES AS AFFECTED BY CULTIVATION AND ORGANIC FERTILIZATION[1]

### E. R. PARKER AND H. JENNY[2]

*California Agricultural Experiment Station*

Growers of citrus and of other fruits frequently have difficulty in obtaining satisfactory penetration of irrigation water into their orchard soils. As a rule, water penetration is good in young orchards, especially in those on land not long in cultivation, but within a few years after the orchard is planted, the infiltration capacity of the soil often declines. To obtain water penetration to a depth of 4 feet, the irrigation time may have to be extended, for example, from an initial period of 8 hours to 24 or 48 hours, or longer. Such unfavorable developments seriously affect the management practices and possibly the performance of the orchards.

Certain plots of an experimental orange orchard of the University of California Citrus Experiment Station, at Riverside, offer a typical illustration. In 1917, when the trees were planted, on land previously used for dry-farmed grain crops, water penetration was excellent. Satisfactory water penetration was generally obtained during the next 10-year period, while the orchard was being farmed uniformly. Cover crops were grown, and no fertilizer was applied during that period. With the inauguration of various fertilizer applications in 1927, it was soon discovered that cultural practices had a marked effect on water infiltration. By measuring the irrigation flow in individual furrows with a calibrated container, L. D. Batchelor and Gordon Surr found [3] that as early as 1931 the various fertilizers had exerted some effects on water penetration. In the plots that had received organic material, the rate of water penetration appeared to be most rapid. It then appeared desirable to study the effects of fertilization and other cultural practices on water penetration in more detail, and in 1935, Batchelor suggested that the authors investigate the changes which had occurred in the infiltration capacity.

## THE EXPERIMENTAL ORCHARD

A detailed description of the experimental orchard of the Citrus Experiment Station has been given by Batchelor, Parker, and McBride (2) and by Parker and Batchelor (6). Suffice it to say here that the orchard comprises 199 plots of 0.22 acre each and is on land of reasonably uniform slope. Each plot (see

fig. 1) consists of nine trees, eight of which are "test" trees, of Washington Navel orange, in a single row, separated from the next plot rows, on either side, by guard rows. The guard trees are of grapefruit and Valencia orange varieties and are slightly larger than the test trees. There are 43 different fertilizer treatments, each replicated four times, essentially at random. A basic control treatment is replicated 25 times. The soil is classified as Ramona loam. The orchard is customarily irrigated by means of furrows nine or ten times a year, at approximately monthly intervals in the dry season. The rainfall averages about 12 inches a year and occurs mostly in the period from November to April. In most years, the plots are cultivated after each irrigation. Fertilizers are broadcast on the irrigated area between test trees and guard trees.



FIG. 1. ARRANGEMENT OF TREES AND IRRIGATION FURROWS IN AN ORCHARD PLOT

The arrangement of trees and furrows in a single plot is shown in figure 1. For the purposes of the present studies, each plot is considered as being divided into a north subplot and a south subplot. Within each subplot the furrows are labeled from 1 to 6, counting from the north. Water flows from east to west in the furrows.

## MEASUREMENT OF WATER INFILTRATION IN THE ORCHARD

Indexes of rates of water infiltration were obtained by means of a "constant-flow method." The flow of water from the irrigation standpipes was adjusted so that a constant amount of water (4 liters per minute) entered the upper end of each furrow. The position of the front of the water stream running down the furrow was then recorded at various time intervals.

Results of determinations made on two individual furrows are shown in figure

2. The positions of the water fronts, as measured from the upper ends of the furrows, are plotted on the ordinate. The abscissa shows the time of the day at which the measurements were taken. The steep, broken-line curve (fig. 2, *A*) is illustrative of a furrow in which the water penetration is very poor. In soils having high infiltration capacity, the water front advances very slowly, and the resulting curve consequently has a gentle slope, as shown by the solid-line curve (fig. 2, )*B*. For purposes of numerical comparison, the "100-foot-time" (the number of hours necessary for the water to travel over the first hundred feet of the furrow) was calculated graphically for each furrow.

In June, 1935, infiltration was measured in two plots (J-40 and M-6) of treatment 2, which received annual applications of 1 pound of nitrogen in the form of urea for every tree; and in two plots (I-16 and K-34) of treatment 42, which,
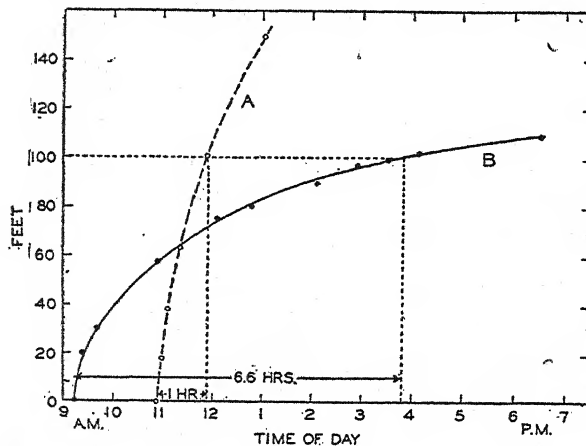


FIG. 2. WATER INFILTRATION IN IRRIGATION FURROWS DIFFERING IN
SOIL PENETRABILITY

Calculated on basis of time necessary for water to flow a distance of 100 feet, when a constant stream (4 liters per minute) enters upper end of each furrow. *A*, rapid movement of water front (100-foot-time, 1 hour) in furrow in soil in which absorption is poor; *B*, slower movement (100-foot-time, 6.6 hours) in soil that absorbs water readily.

in addition to urea, received manure and were also planted to winter cover crops. In plots I-16 and K-34 the total nitrogen applied per tree annually was 3 pounds, half from urea and half from manure.

Infiltration studies were also conducted at that time in two plots of a dry-farmed area adjacent to the citrus orchard. This field has been idle during a large period of its history and has never been fertilized. It is probable that the soil conditions correspond closely to those of the orchard prior to the planting of the trees.

A summary of the infiltration measurements, expressed as 100-foot-time, is given in table 1. The differences are very marked. The soil of the orchard plots receiving manure and having cover crops absorbed water more than three times as readily as that of the plots receiving urea alone. The soil of the dry-farmed area absorbed water much more rapidly than that of either of these

orchard plots. If the infiltration capacity of the dry-farmed soil is indicative of the original infiltration capacity of the soil in the orchard, it is evident that the management practices in the orchard drastically reduced the capacity of the soil for taking water.

Infiltration measurements were repeated on a wider scale in August, 1938. Six fertilizer treatments, of four plots each, were investigated. The following fertilizer applications have been made annually since 1927:

Treatment 2, urea (1 pound N per tree)
Treatment 18, urea (1 pound N per tree) plus cover crop
Treatment 19, manure (3 pounds N per tree)
Treatment 30, manure (1 pound N per tree)
Treatment 31, manure (1 pound N per tree) plus cover crop
Treatment 42, urea plus manure plus cover crop (3 pounds N per tree—1.5 pounds from urea and 1.5 pounds from manure).

TABLE 1

*Water infiltration in orchard plots receiving treatments 2 and 42, and in dry-farmed area*
*(June, 1935)*

| TREATMENT | MEAN 100-FOOT-TIME* PER FURROW | DEGREES OF FREEDOM UPON WHICH ERROR IS BASED |
|---|---|---|
| | *hours* | |
| 2. Urea only.......................... | 1.60 ± 0.32† | 17 |
| 42. Urea + manure + cover crop...... | 5.24 ± 0.56† | 17 |
| None (dry-farmed area).............. | 27.17 ± 2.79 | 4 |

\* The time necessary for a stream of 4 liters of water per minute to flow 100 feet in the furrows.

† Standard error of mean after elimination, by applications of analysis of variance, of variation between replicates and between furrows within plots.

It is to be noted that these treatments are made up of various combinations of urea, manure, and cover crops, in the absence of mineral fertilizers. Parker and Batchelor (7) have observed that in this orchard neither trees nor cover crops will produce satisfactory yields over an extended period of time without applications of nitrogenous fertilizer.

A graphic summary of the mean results for the individual furrows in the subplots of the variously treated plots is presented in figure 3. The values for water infiltration, expressed as 100-foot-time, are plotted on the ordinate. On the abscissa are indicated the six furrows of a subplot. Large differences in the effects of the various treatments are evident. The divergence is especially pronounced between the plots without organic matter (treatment 2) and the plots receiving treble amounts of nitrogen from manure (treatment 19). It is also evident that the furrows of any one treatment differ greatly in their infiltration capacities, but that the relative behavior of the furrows is generally similar in the different treatments. In order to study the effects of the treatments and the relations of the furrows to one another, statistical analysis was used.
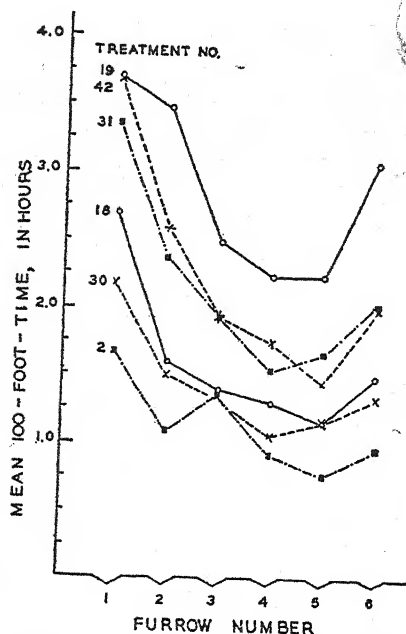
FIG. 3. WATER INFILTRATION IN RELATION TO CULTURAL TREATMENT OF PLOTS AND LOCATION OF FURROWS IN SUBPLOTS

Furrows are numbered from north to south in each subplot (see fig. 1). See text for description of treatments.

TABLE 2

*Analysis of variance of measurements of water infiltration in furrows, based on 100-foot-time, as affected by six cultural treatments in the orchard (August, 1938)*

| SOURCE OF VARIATION | DEGREES OF FREEDOM | MEAN SQUARE | F |
|---|---|---|---|
| Between cultural treatments...................... | 5 | 19.65 | 19.65** |
| Between plots within treatments.................. | 18 | 1.00 | |
| Between furrows within subplots.................. | 5 | 14.16 | 56.64** |
| Interaction, furrows × subplots.................. | 235 | 0.25 | |
| Between north and south subplots................ | 1 | 1.73 | 5.19* |
| Interaction, subplots × plots.................... | 23 | 0.34 | |
| Total........................................... | 287 | | |

* Significant ($P < 5$ per cent; $> 1$ per cent).
** Highly significant ($P < 1$ per cent).

The infiltration values of the six treatments (of four plots each, each plot comprising two subplots of six furrows each) were subjected to analysis of variance (4, 9). This analysis (table 2) is based on the unit 100-foot-time of the individual furrows. As regards the effect of cultural treatments, the differences

in water infiltration are highly significant. The mean readings for the various treatments are listed in descending order of rate of water penetration, in table 3, where the successive differences between means are also given. The least significant differences between the means of any two treatments would not be expected, by chance, to be equal to or greater than 0.123 hour in more than 5 per cent of the cases, and a mean difference of 0.170 hour would not be expected in more than 1 per cent of the cases. It is apparent that treatment 2 (urea, without cover crop) is very significantly poorest ($P < 1$ per cent) in water infiltration. Treatments 18 (urea plus cover crop) and 30 (light application of manure) are next poorest. These two treatments differ slightly but significantly ($P < 5$ per cent), the furrows of treatment 18 being somewhat more permeable, but both are markedly and very significantly poorer in water infiltration than treatments 31 (light application of manure plus cover crop) and 42 (moderate

### TABLE 3

*Effect of cultural treatments of orchard plots on water infiltration (August, 1938)*

| TREATMENTS* IN DESCENDING ORDER OF RATE OF WATER PENETRATION IN FURROWS | 100-FOOT-TIME | |
|---|---|---|
| | Mean per furrow | Successive differences between means† |
| | *hours* | *hours* |
| 19. Manure (3 pounds N)............................ | 2.866 | |
| | | 0.631 |
| 42. Urea (1.5 pounds N) + manure (1.5 pounds N) + cover crop..................................... | 2.235 | |
| | | 0.083 |
| 31. Manure (1 pound N) + cover crop.............. | 2.152 | |
| | | 0.563 |
| 18. Urea (1 pound N) + cover crop................. | 1.589 | |
| | | 0.162 |
| 30. Manure (1 pound N)........................... | 1.427 | |
| | | 0.313 |
| 2. Urea (1 pound N)............................... | 1.114 | |

* Descriptions show, in parentheses, the total nitrogen applied per tree annually in each treatment.

† Least significant differences between any two means: 0.123 at 5 per cent probability; 0.170 at 1 per cent.

application of manure plus urea and cover crop), which are very similar. However, the water infiltration in plots receiving treatment 19, which consisted of heavy applications of manure, is much, and very significantly, more rapid than in any of the other treatments.

These results clearly indicate that the water infiltration in the various plots is directly related to the quantity of organic matter applied (5, 8). Particular interest attaches to the comparisons between plots treated with manure and those in which the cover crops are the sole source of organic matter. It is sometimes assumed that a beneficial influence on water penetration may be attributed to the root system of the cover crop, the decayed roots providing a multitude of channels that facilitate the percolation of water. The penetration results obtained with treatments 18, 19, and 30 cast doubt upon this belief. The light manure applications (treatment 30), involving surface applications of

organic matter which are not cultivated to depths of more than 4 or 5 inches, were nearly as effective as cover crops (treatment 18). The heavy applications of manure (treatment 19) were more effective. These findings suggest that the problem of water infiltration, as conditioned by organic matter, is closely associated with processes occurring in the upper portions of the soil.

It was noted in figure 3 that prominent differences were recorded in infiltration capacities for various furrows, and that the furrows in the various treatments are remarkably consistent in this respect. The analysis of variance shows that the differences in water infiltration among the means of individual furrows of the subplots of all the treatments are highly significant. The mean 100-foot-time for the furrows, arranged in descending order of water penetration, is presented in table 4. The differences necessary for significance between any two means are 0.201 at the 5 per cent level and 0.265 at the 1 per cent level.

TABLE 4

*Water infiltration in individual furrows of all subplots of the six orchard treatments\**
*(August, 1938)*

| FURROWS, IN DESCENDING ORDER OF WATER INTAKE† | 100-FOOT-TIME | |
|---|---|---|
| | Mean per furrow | Successive differences between means‡ |
| | *hours* | *hours* |
| 1 | 2.879 | |
| | | 0.781 |
| 2 | 2.098 | |
| | | 0.290 |
| 6 | 1.808 | |
| | | 0.071 |
| 3 | 1.737 | |
| | | 0.268 |
| 4 | 1.469 | |
| | | 0.075 |
| 5 | 1.394 | |

\* Each of the six treatments was replicated four times; there were, therefore, 48 values for each furrow.

† Furrows were numbered from north to south in each of the 48 subplots (see fig. 1).

‡ Least significant differences between any two means: 0.201 at 5 per cent probability; 0.265 at 1 per cent.

It is apparent that, on the average, furrow 1, immediately south of the tree rows, absorbs water much more readily than any other furrow. The differences are highly significant ($P < 1$ per cent). Furrow 2 is next in rank, and its increased intake over furrow 6 is also highly significant. Furrows 3 and 6 do not appear significantly different, but both differ very significantly from all other furrows. Furrows 4 and 5 are very significantly the poorest in their ability to absorb water, but they do not differ significantly from each other.

No explanation for the difference between the two tree furrows (nos. 1 and 6) can be offered from the data at hand. It might be mentioned, however, that in other orchards of the Citrus Experiment Station, where the furrows are oriented in a north-to-south direction, the two tree furrows have equal infiltration capacities.

Differences between the north and the south sides of the plots also are suggested by the analysis of variance. The mean values per furrow for all treatments

are 1.98 hours on the north subplots, and 1.82 hours on the south subplots. The difference, though small, might be expected by chance in less than 5 per cent of similar experiments in this orchard. It may be attributed to an interaction effect between guard trees (which are somewhat larger than the plot trees) and furrow number, or to differential compaction by farm equipment.

### TEXTURAL CHARACTERISTICS OF THE SOILS

The clay content of the soils of the four plots of treatment 2 and of treatment 42 of the fertilizer experiment, and also of the dry-farmed area, was determined during the summer of 1935 by the hydrometer method of Bouyoucos (3). Although this technique does not give the percentage of clay to a very high degree of precision, it was considered to be sufficiently accurate for measuring the relative variability of soil texture. From the irrigated area of each plot numerous samples were collected at 3-inch horizons, to a depth of 24 inches. The mechanical
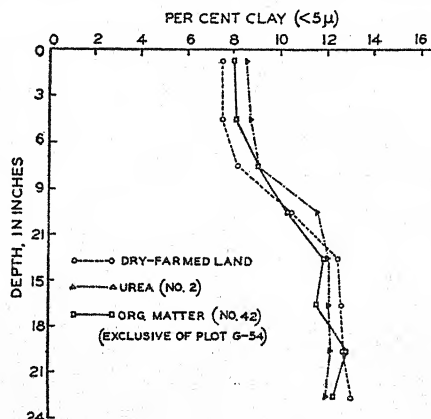


FIG. 4. AVERAGE CLAY CONTENT OF SOILS GIVEN TREATMENTS 2 AND 42, AND OF DRY-FARMED AREA, IN RELATION TO DEPTH

analysis was run on composites; that is, within each plot the samples belonging to a given depth interval were combined. According to the results obtained, the average clay content of the surface 6 inches is generally about 8 per cent. With increasing depth the clay content augments until it reaches a value of 12 to 13 per cent at a depth of 24 inches (fig. 4). All plots follow this pattern very closely, except plot G-54 of treatment 42, which has a higher clay content throughout the soil profile, varying from 13 per cent in the surface soil to about 18 per cent in the subsoil.

Comparison of the clay content of the dry-farmed area with that of the orchard furnishes no support of the theory that irrigation and other operations conducted in the orchard have produced a zone of clay accumulation. Inasmuch as the values for silt and sand follow trends which are in harmony with that of the clay data, we may conclude that textural differences among the treatment plots do not account for the profound differences observed in water infiltration.

Moisture equivalents were next determined for the top 12-inch layer of the

irrigated soil.  Within each plot, eight samples were determined individually, so that the average moisture equivalents of treatments 2 (12.07 per cent) and 42 (13.68 per cent) are each representative of 32 samples.  The average values of the individual plots are given in table 5.  Similar samples from the dry-farmed area gave a mean value of 11.63 per cent.  This area is in close proximity to plot M-6, which has an almost identical moisture equivalent.  The organic matter plots (treatment 42) have slightly higher values for this index.

TABLE 5

*Moisture equivalents of surface soils (0- to 12-inch depth) of plots given different fertilizer treatments*

| TREATMENT 2* | | TREATMENT 42† | |
|---|---|---|---|
| Plot | Moisture equivalent | Plot | Moisture equivalent |
| | *per cent* | | *per cent* |
| D-22 | 12.02 | E-24 | 12.98 |
| F-38 | 12.12 | G-54 | 15.39 |
| J-40 | 12.25 | I-16 | 13.21 |
| M-6 | 11.88 | K-34 | 13.12 |
| Average | 12.07 | Average | 13.68 |

* Urea supplying 1 pound of nitrogen per tree annually; no cover crop.

† Urea and manure, each supplying 1.5 pounds of nitrogen per tree annually, with winter cover crop.

### RESISTANCE VALUES

Observation in the citrus orchard indicated a correlation between water infiltration and the amount of effort necessary to drive the soil-sampling tube into the ground.  An attempt was made to establish this energy relationship on a quantitative basis as follows:

The hammer which accompanies the soil-sampling tube (King or California type) weighs 16 pounds.  When this hammer is lifted 1 foot above the tube, it possesses a potential energy of 16 foot-pounds.  Dropping the hammer on the tube will drive the latter a certain distance, say $x$ inches, into the soil.  Dividing 16 by $x$ gives the average resistance value expressed as foot-pounds per inch of soil for the depth interval of $x$ inches.

The resistance value varies with the moisture content of the soil.  To ensure comparable conditions, all measurements were made a few days after irrigation, when the soil moisture was at approximate field capacity.  Within each subplot eight horizons, each of 3-inch intervals, to a 24-inch depth, were investigated. Though the individual determinations are variable, the averages reveal outstanding differences among the plots of the various fertilizer treatments.

An analysis of variance of the data for treatments 2 and 42 of the fertilizer experiments, presented in table 6, is based on resistance values determined for 3-inch intervals of soil to a depth of 24 inches.  The mean values for treatments 2 (urea only) and 42 (urea, manure, and cover crop) are found to be very signifi-

cantly different. The means of 512 values are as follows, in foot-pounds per inch: for treatment 2, 28.36; for treatment 42, 23.03; the difference, 5.33.

The average resistance values for successive 3-inch horizons of the organic matter plots (treatment 42) and of the urea plots (treatment 2) are shown in table 7. A distinct zone of high resistance at a depth of about 6 to 12 inches is apparent with both orchard treatments. The presence of a zone of compaction in the orchard is therefore definitely indicated. This layer of high friction is especially pronounced for the plots that do not receive manure and cover crops. Apparently, these organic amendments exert an ameliorating influence on the consistency of the soil. It is of further especial interest to note that the differentiation between the two orchard treatments exists only in the surface soil,

TABLE 6

*Analysis of variance of resistance values and core weights in orchard plots given treatments 2 and 42*

Resistance values in foot-pounds per inch of soil; core weights in grams per cubic centimeter

| SOURCE OF VARIATION | DEGREES OF FREEDOM | RESISTANCE VALUES | | CORE WEIGHTS | |
|---|---|---|---|---|---|
| | | Mean square | F | Mean square | F |
| Between treatments | 1 | 7,285 | 7.15* | 0.8281 | 15.57** |
| Between plots within treatments | 6 | 1,019 | | 0.0532 | |
| Between sampling positions | 15 | 1,824 | 22.14** | 0.0353 | 2.78** |
| Error for testing means of positions | 945 | 82 | | 0.0127 | |
| Between horizons | 7 | 18,067 | 217.39** | 1.6360 | 107.63** |
| Error for testing means of horizons | 889 | 83 | | 0.0152 | |
| Interactions | 994 | 97 | | 0.0149 | |
| Total | 1,023 | | | | |

* Significant ($P$ <5 per cent; >1 per cent).
** Highly significant ($P$ <1 per cent).

to a depth of 12 inches. From 12 to 24 inches, the two treatments have almost identical resistance values.

In comparing the mean resistance of the soils of the two treatments at any single horizon (and also in comparing the means of a single treatment at different horizons), the minimum differences necessary for significance between mean values are 3.159 at the 5 per cent level and 4.159 at the 1 per cent level. It may be seen from table 7 that differences between the two orchard treatments, at the same horizon, exceed those needed for high significance, to a depth of 12 inches. Below 12 inches, the differences are negligible.

Table 7 also shows the mean resistance values for horizons in the dry-farmed area. The values are small and rather uniform. When mean resistance values for the dry-farmed area and for the plots receiving the two orchard treatments

2 and 42 are compared (table 8), marked differences are revealed. The difference between any two of the means presented in this table is obviously significant in view of the standard errors involved. The difference between the mean of the resistance energies in the dry-farmed area and the mean of similar values for either orchard treatment is conspicuously greater than the mean difference be-

### TABLE 7

*Mean resistance values and core weights at different horizons in soils given different orchard treatments and in dry-farmed area*

| LOCATION AND TREATMENT | 0–3 INCHES | 3–6 INCHES | 6–9 INCHES | 9–12 INCHES | 12–15 INCHES | 15–18 INCHES | 18–21 INCHES | 21–24 INCHES |
|---|---|---|---|---|---|---|---|---|
| *Mean resistance values (foot-pounds per inch)* | | | | | | | | |
| Orchard (treatment 2)*.......... | 7.26 | 29.78 | 45.71 | 47.96 | 32.79 | 24.46 | 19.68 | 19.27 |
| Orchard (treatment 42)*......... | 2.98 | 16.39 | 28.80 | 38.45 | 32.59 | 24.20 | 20.37 | 20.44 |
| Difference†..................... | 4.28 | 13.39 | 16.91 | 9.51 | 0.20 | .0.26 | −0.69 | −1.17 |
| Mean....................... | 5.12 | 23.09 | 37.26 | 43.20 | 32.69 | 24.33 | 20.02 | 19.85 |
| Dry-farmed area (no treatment)‡. | 2.26 | 4.18 | 7.16 | 11.84 | 10.40 | 9.50 | 9.42 | 9.41 |
| *Mean core weights (grams per cubic centimeter)* | | | | | | | | |
| Orchard (treatment 2)*.......... | 1.51 | 1.72 | 1.74 | 1.71 | 1.60 | 1.55 | 1.49 | 1.51 |
| Orchard (treatment 42)*......... | 1.26 | 1.57 | 1.67 | 1.70 | 1.63 | 1.55 | 1.47 | 1.52 |
| Difference§.................... | 0.25 | 0.15 | 0.07 | 0.01 | −0.03 | 0.00 | 0.02 | −0.01 |
| Mean ....................... | 1.385 | 1.645 | 1.705 | 1.705 | 1.615 | 1.550 | 1.480 | 1.515 |
| Dry-farmed area (no treatment)‡. | 1.35 | 1.31 | 1.50 | 1.52 | 1.38 | 1.39 | 1.36 | 1.40 |

\* Each mean is based on 64 determinations.

† Significant values: 3.159 at 5 per cent level; 4.159 at 1 per cent level.

‡ Each mean is based on 8 determinations.

§ Significant values: 0.043 at 5 per cent level; 0.056 at 1 per cent level.

### TABLE 8

*Mean resistance values and core weights in plots of two orchard treatments and in dry-farmed area*

| LOCATION AND TREATMENT | MEAN RESISTANCE VALUE, FOOT-POUNDS PER INCH | MEAN CORE WEIGHT, GRAMS PER CUBIC CENTIMETER | DEGREES OF FREEDOM UPON WHICH ERROR IS BASED |
|---|---|---|---|
| Orchard (treatment 2)......... | 28.365 ± 1.037* | 1.604 ± 0.0049* | 735 |
| Orchard (treatment 42)........ | 23.031 ± 1.037* | 1.547 ± 0.0049* | 735 |
| Dry-farmed area (no treatment). | 8.022 ± 0.278* | 1.400 ± 0.0119* | 49 |

\* Standard error of mean from residual error of analyses of variance.

tween the two fertilizer plots. From table 7 it may be seen that the difference between the resistance values in the orchard soil and in the dry-farmed area is most pronounced at a depth of 6 to 12 inches. It is apparent that orchard practices have adversely affected the consistency of the soil, as well as its infiltration capacity, in the orchard plots.

Measurements of water infiltration in the orchard showed a characteristic

behavior of the various furrows (fig. 3).   In the furrows adjacent to the tree rows, the water penetration was much better than in those near the center of the plots.   In the light of the observed negative correlation between rate of water infiltration and resistance values, it appeared promising to examine the behavior of the furrows in greater detail.   Accordingly, resistance values for two positions were determined in each of the furrows numbered 1, 4, and 6 for two whole plots of each of treatments 2 and 42.   Observations were made for 3-inch horizons to a depth of 24 inches.   The mean resistance values of each furrow for all horizons in all plots are as follows, in foot-pounds per inch: for furrow 1 (south of tree rows), 22.85; for furrow 6 (north of tree rows), 20.95; and for furrow 4 (center of subplots), 29.04.

An analysis of variance, based on an error having 62 degrees of freedom, discloses that, in contrast to the water-infiltration data presented in table 4, the resistance values of the two tree furrows, nos. 1 and 6, do not differ materially. On the other hand, resistance values of the center furrow are significantly greater, and hence are in harmony with the lower water-infiltration capacity of that furrow.

## CORE OR VOLUME WEIGHTS

The presence of a zone of soil compaction in the orchard, as suggested by the resistance values, was confirmed by a study of volume weights (apparent densities).   The hollow sampling tube, which has a cutting edge with an interior diameter of 2.2 cm., was driven 3 inches into the soil and then pulled out carefully.   The core of soil inside the tube was removed, placed in a can, dried at 105° C., and weighed.   The weight of the 3-inch core, expressed as grams per cubic centimeter of volume, closely corresponds to the volume weight or apparent density as determined by the paraffin immersion technique.   In order to emphasize the difference in technique, the term "core weight," instead of "volume weight," is used throughout the discussion.

Samples were collected in this manner to a depth of 24 inches.   Eight samples for each horizon were taken in each subplot, a procedure yielding 64 samples at each of eight horizons for the four plots of each of orchard treatments 2 and 42.   Eight samples were also taken for each horizon of the dry-farmed area.

An analysis of variance for the data of treatments 2 and 42 is given in table 6.   The mean core weights of the treatments differ very significantly.   The means of 512 core weights for each orchard treatment are as follows: for treatment 2, 1.604; for treatment 42, 1.547; with a difference of 0.057.

The mean values of the core weights for each horizon of treatments 2 (urea alone) and 42 (urea, manure, and cover crop), are given in table 7.   Comparison with the resistance values reveals some striking similarities.   In fact, the correlation coefficient between core weight and resistance energy, based on 1,024 determinations in the orchard plots, is +0.6422.   The averages of the core weights show a zone of high density at a depth of 3 to 12 inches, which agrees closely with the zone of high resistance values.   This region of compaction is definitely more pronounced in the plots which do not receive organic matter in the form of manure and cover crop.

In comparing the mean core weights of the two treatments at the same horizon (and also in comparing the means of a single treatment at different horizons), the difference necessary for significance between any two such means is 0.043 at the 5 per cent level and 0.056 at the 1 per cent level. Between the two treatments, the core weights are obviously significantly different at the same level to a depth of 9 inches. Below that level they are variable and not significantly different.

Table 7 also shows the mean core weights for the horizons of the dry-farmed area to a depth of 24 inches. Comparisons of the mean values for the dry-farmed area with the mean values for the two orchard treatments indicate that the soil is more dense in the orchard at each level. Mean values for the core weights at all horizons are given in table 8. In view of the standard errors involved, it is obvious that the mean core values for the dry-farmed area are significantly less than the mean values of either of the orchard treatments. This is in agreement with the observations on water infiltration and resistance values.

In view of the characteristic behavior of individual furrows in the orchard with respect to water infiltration, a search was made for corresponding relations with core weights. As in the case of the resistance values, the tree furrows, nos. 1 and 6, and a center furrow, no. 4, of two plots of treatments 2 and 42 were selected for this phase of the study. The samples in each location were taken in 3-inch horizons to a depth of 24 inches.

The mean values, including all plots and horizons, are as follows: for tree furrow 1, 1.48; for tree furrow 6, 1.48; and for center furrow 4, 1.52. The two tree furrows are equal in core weight, but the center furrow is very significantly different ($P < 1$ per cent) from either tree furrow, as determined by an analysis of variance having 62 degrees of freedom for error. The difference in core weights is small, however, in comparison with the marked differences observed in the values for water infiltration and for resistance.

### COMPACTION AND CULTIVATION EXPERIMENTS

The data on infiltration, resistance values, and core weights for the orchard plots and for the adjacent dry-farmed area strongly indicate that operations in the orchard have been very detrimental to the soil. With no direct evidence on the effect of the soil-management practices involved, it was decided to conduct experimental compaction and cultivation tests on the dry-farmed area. The following types of treatment were therefore applied: (a) tractor compaction, with a track-type tractor, of soil in dry condition (at or below permanent wilting percentage), and also of soil in wet condition (near field capacity); (b) disking of soil in dry condition and in wet condition as above.

### Arrangement and preliminary preparation of plots

The dry-farmed area of the present experiments is situated in field S5, block A, and adjoins the experimental orchard. In July, 1935, when these experiments were started, the area had a good stand of tall dry weeds. These were mowed close to the ground and removed. The field was then disked and the plots were laid out in such a way that they had the same slope as that of orchard plot M-6, namely, 1.73 feet per 100. The arrangement of plots is shown in

figure 5. Each plot was 12 feet wide and nearly 200 feet long, and each contained three furrows about 4 inches deep. The check plots were replicated four times, but later one check plot (no. 8) was inadvertently used for other purposes. The treated plots were not replicated.

### Experiments on dry soil

On July 29–30, 1935, plot 2 was worked for about 8 hours with a 2-ton caterpillar tractor. The surface soil became disintegrated and assumed the properties of an almost impalpable powder. Dust clouds became so menacing that the treatment had to be discontinued after completion of 200 passages of the tractor.
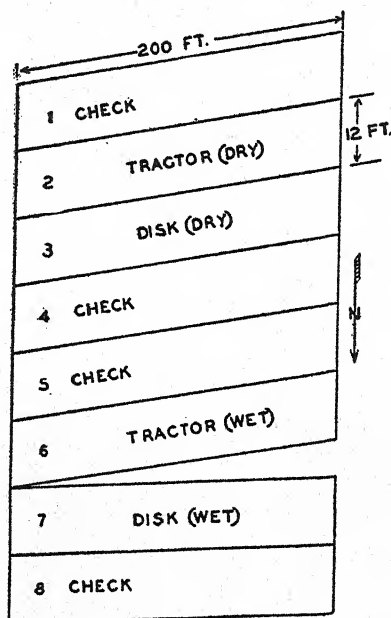


FIG. 5. ARRANGEMENT OF THE PLOTS OF THE COMPACTION AND CULTIVATION EXPERIMENTS IN THE DRY-FARMED AREA

Every part of the plot was traversed 33 times by the tracks of the tractor. The compacted area was then furrowed out in the manner mentioned above.

On July 30, 1935, the dry soil of plot 3 was disked. Fifty passages with a wide double disk, such as that used for turning in cover crops, were made over the area. The 22-inch blades of the disk penetrated about 6 inches. After the plot had been disked, the furrows were drawn in such a way that they were not located in the tracks of the tractor which drew the disk.

On July 31 and August 1, 1935, *all* plots were irrigated and subjected to measurements of water infiltration. On August 5 and 6, resistance values were obtained in the checks and in the dry-worked plots (nos. 2 and 3), and samples were taken for determination of core weights. Two or three sampling locations were used in each furrow, and samples were taken in increments of 3 inches to a depth of 2 feet.

Because of the high rate of water infiltration in the check plots, the calculation of the 100-foot-time (previously used as a criterion) would require excessive extrapolation and was not considered feasible. In these studies water infiltration is therefore expressed as the distance which the front of a constant stream of water (4 liters per minute) traveled in the furrow in 5 hours' time. These

TABLE 9

*Effect of compaction and cultivation of dry soil on water infiltration in the first irrigation after treatment (July 31 to August 1, 1935)*

| PLOT NO. AND TREATMENT | 5-HOUR DISTANCE* | | | |
|---|---|---|---|---|
| | Furrow 1 | Furrow 2 | Furrow 3 | Mean |
| | ft. | ft. | ft. | ft. |
| 1. Check (no treatment)............. | 66 | 60 | 78 | 61 |
| 4. Check (no treatment)............. | 53 | 51 | 58 | |
| 2. Tractor-compacted............... | 138 | 210 | 174 | 174 |
| 3. Disked........................ | 165 | 174 | (96)† | 170 |

* The distance a stream of water (4 liters per minute) flows in 5 hours.
† Furrow partially outside of disked strip. Not included in mean.
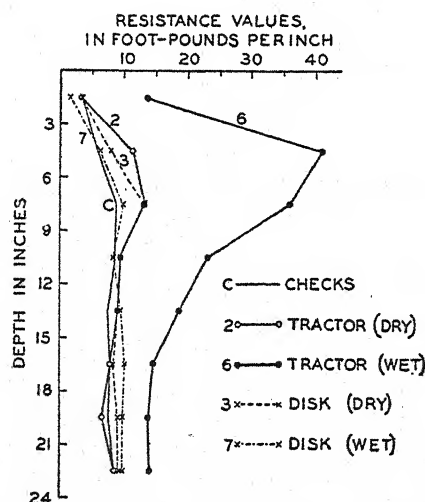


FIG. 6. RESISTANCE VALUES OF SOIL IN PLOTS OF THE COMPACTION AND CULTIVATION EXPERIMENTS

Values expressed as foot-pounds of energy necessary to drive the soil tube 1 inch into the soil.

distances, for the irrigation of July 31 to August 1, 1935, are assembled in table 9.

The effects of treatment are very striking. The tractor and the disk treatments on dry soil were both very detrimental to water infiltration. In 5 hours, water traveled nearly three times as far in the furrows of the treated plots as

in those of the adjacent check plots, a condition which reflects poor water penetration in the former. The profound decrease in water infiltration was accompanied by changes in resistance values and core weights. This is clearly seen from figures 6 and 7, which show an appreciable difference in the values
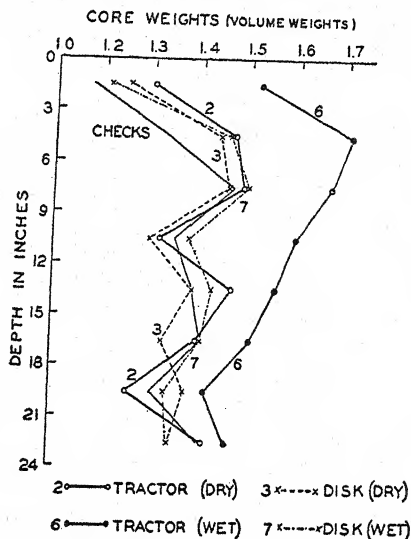


FIG. 7. CORE OR VOLUME WEIGHTS OF SOIL IN PLOTS OF THE COMPACTION AND CULTIVATION EXPERIMENTS

TABLE 10

*Mean resistance values\* and core weights†, to a depth of 9 inches, of soil of the compaction and cultivation experiments (August, 1935)*

| PLOT NO. AND TREATMENT | RESISTANCE VALUE‡ | CORE WEIGHT‡ |
|---|---|---|
| 1. Check | 5.30 ± 0.521 | 1.34 ± 0.027 |
| 2. Dry soil, tractor-compacted | 9.19 ± 0.887 | 1.42 ± 0.017 |
| 3. Dry soil, disked | 8.52 ± 0.480 | 1.38 ± 0.003 |
| 4. Check | 4.55 ± 0.407 | 1.27 ± 0.033 |
| 5. Check | 5.04 ± 0.062 | 1.29 ± 0.023 |
| 6. Wet soil, tractor-compacted | 30.15 ± 1.131 | 1.63 ± 0.016 |
| 7. Wet soil, disked | 5.93 ± 0.498 | 1.39 ± 0.018 |
| 8. Check | 7.90 ± 0.455 | 1.37 ± 0.023 |

\* Foot-pounds of energy necessary to drive the sampling tube into the soil a distance of 1 inch.

† Grams per cubic centimeter.

‡ Means and standard errors of the means.

of the surface soils (0 to 9 inches) between the means of all the check plots and the two plots (nos. 2 and 3) which were treated while in a dry condition. Likewise, the data in table 10 reveal a significant compaction, as judged from comparison of the resistance values and core weights for the 0- to 9-inch horizon of dry-treated plots and adjacent check plots.

## Experiments on wet soil

A few days after the irrigation of August 1, 1935, the moist soil of plot 6 was subjected to compaction with the tractor. When the entire plot had been passed over 33 times, the plot had assumed a concave shape, the center portion being depressed 7 inches below the original surface. Plot 7 was disked the following day. Fifty passages were made and special care was taken that the tractor which pulled the disk should always follow the same track, so that the furrows would lie only in the disked portion of the plot. Resistance values were obtained on August 9 to 12, and samples for core-weight determinations were taken at that time. On August 13, 1935, while the soil was still moist, the plots were furrowed and subjected to another irrigation. During this irrigation measurements of water infiltration were made.

In conformity with the experiments on dry soil, the distance which the front of the water stream (4 liters per minute) traveled in the furrow during 5 hours was taken as an index of water infiltration. The 5-hour distance of each furrow

TABLE 11

*Effect of compaction and cultivation of wet soil on water infiltration in the first irrigation after treatment (August 13, 1935)*

| PLOT NO. AND TREATMENT | 5-HOUR DISTANCE | | | |
|---|---|---|---|---|
| | Furrow 1 | Furrow 2 | Furrow 3 | Mean |
| | *ft.* | *ft.* | *ft.* | *ft.* |
| 5. Check (no treatment)............. | 93 | 54 | 96⎫ | |
| 8. Check (no treatment)............. | 78 | 114 | 117⎭ | 92 |
| 6. Tractor-compacted............... | 1,550* | ... | 1,210* | 1,380 |
| 7. Disked†......................... | 81 | 60 | 72 | 71 |

* By extrapolation.

† See text for comment on infiltration during subsequent irrigations of this plot.

of each plot is given in table 11. It should be noted that the absolute values in table 11 cannot be compared with those of table 9 because the data presented in the latter table were obtained during the irrigation of dry soil, whereas those of table 11 were obtained during the irrigation of moist soil. The results of the compaction of wet soil by the tractor (plot 6) are very striking. The soil was made so impervious that the water speedily ran down the furrow and covered the entire distance of nearly 200 feet in less than 1 hour. In contrast to the effects of the tractor, the action of the disk on wet ground apparently did not produce any harmful effect in the first irrigation. *It is very important to note,* however, that subsequent irrigations on the wet-disked plot (no. 7), after it had dried out thoroughly, did reveal a reduction in water permeability, which was, however, not so pronounced as the effect of intensive disking of dry soil (see fig. 9).

Examination of mean resistance values and core weights of the plots worked while in a wet condition (table 10) corroborates the trends of the infiltration

figures for the first irrigation after the soil manipulation. Comparison between check plots and disked plot 7 fails to show any marked *immediate* effect of disking of wet ground. On the other hand, very formidable compaction resulted on plot 6, which was treated with the tractor. Compaction was most pronounced in the surface soil, but extended to a depth of at least 24 inches.

In figures 6 and 7, it appears that the patterns for resistance values and core weights obtained in plot 6 are very similar to the patterns for similar data obtained in the orchard soils. This suggests that the low rates of water infiltration observed in the orchard, and the soil conditions associated with them, are influenced by compaction due to the use of tractors or other equipment on moist soil. It is evident, however, that dry soil is also adversely affected by such treatment.

### RESTORATION OF DETERIORATED SOIL

In view of the detrimental effects of intensive traffic and cultivation that developed in the compaction and cultivation experiments, and that appear to exist in the orchard, the question immediately arises: By what means is it possible to restore the water-infiltration capacity of overcultivated and physically deteriorated soils?

A partial answer is provided by the observations reported above on the effects of various orchard treatments, which show that the application of liberal amounts of manure and the turning under of cover crops assist in maintaining good water penetration. Of additional interest is the suggestion advanced by W. R. Schoonover, of the California Agricultural Extension Service, that reduction in amount of cultivation will bring about a rehabilitation of soil structure and improve water penetration.[4] This suggestion, which has been widely adopted in practice, was tested on the compaction and cultivation plots.

Subsequent to the infiltration measurements in August, 1935, all the plots were reirrigated. Then mustard (*Brassica nigra*) was sown on the wet soil. This crop grew vigorously in the check plots, but poor stands and poor growth resulted on the treated plots. Growth was especially poor on plot 6, which was tractor-compacted while the soil was moist (see fig. 8). In November, 1935, when the soil had dried, the mustard plants were cut off and removed without disturbing the soil. The plots were then irrigated again in the same furrows, and the water infiltration was measured in the same manner as before. Mustard was sown again after the irrigation. This second crop was left on the land throughout the ensuing rainy period (the winter of 1935–36). Good growth was obtained on the check plots, and somewhat improved growth resulted on the treated plots. In order to ensure the removal of water from the

[4]Frank Hinckley has gone even further and eliminated cultivation entirely in his citrus orchard near Redlands, California (1). For about 20 years his orchard has not been plowed or disked. The soil has been kept bare by scraping off the weeds with a hoe. A comparable practice has been adopted in recent years by a considerable number of citrus growers in California, who do not cultivate, but keep their orchards free of grasses and other herbaceous plants by spraying young plants with oil. The practice has frequently improved the physical condition of the soil.

soil during the following dry season, the plants were not harvested until the end of the summer of 1936. In October of that year, the crop was removed as before, and water penetration in the dried soil of the original, undisturbed
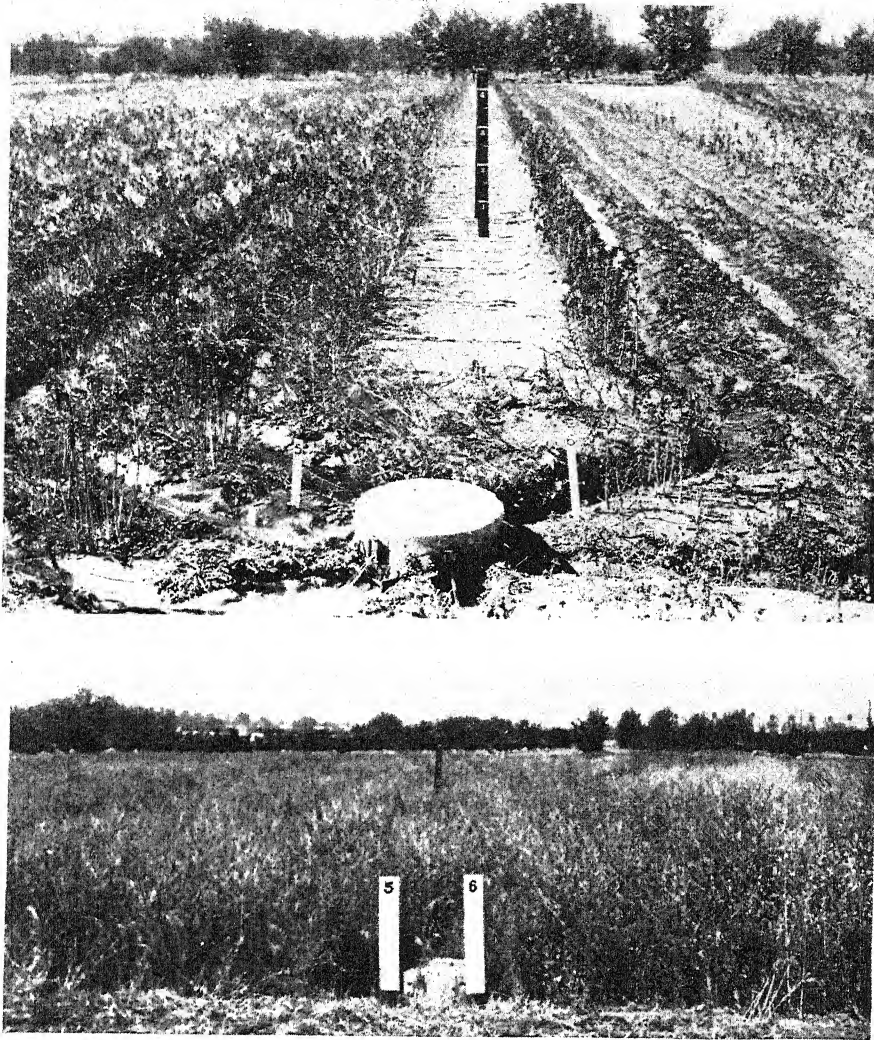


FIG. 8. TOP: REDUCTION IN GROWTH OF *Bassica nigra* AND WEEDS, CAUSED BY TRACTOR COMPACTION OF WET SOIL—OCTOBER, 1935

BOTTOM: GROWTH OF MUSTARD AND VOLUNTEER WEEDS DURING WINTER OF 1943–44, 8 YEARS AFTER TREATMENT

Left, check plot 5; right, wet-compaction plot 6.

furrows was again measured. This last-mentioned procedure of sowing, harvesting, and irrigating of dry soil was repeated annually until November, 1941, and again in 1943. No operations were performed in 1942.

Analysis of the infiltration values for the period 1935–1943 indicates two

independent variations: The first is an unexplainable variation in water penetration in all plots (tractor-compacted, disked, and check), from year to year. The mean values for the check plots are as follows:

| Date of measurement | 5-hour distance, in feet |
|---|---|
| August, 1935 | 62 |
| November, 1935 | 125 |
| October, 1936 | 98 |
| August, 1937 | 49 |
| August, 1938 | 39 |
| August, 1939 | 114 |
| October, 1940 | 88 |
| October, 1941 | 45 |
| November, 1943 | 35 |

Fluctuations in the other plots paralleled these.
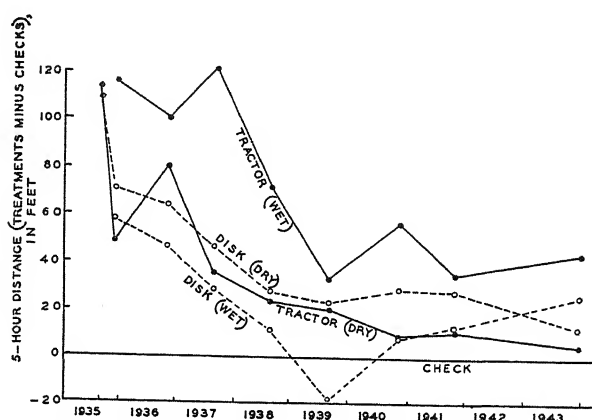


FIG. 9. RESTORATION OF THE WATER-INFILTRATION CAPACITY OF PLOTS COMPACTED BY TRACTOR TRAFFIC OR BY INTENSIVE DISKING

The increases in 5-hour distances of the mean value of treated plots over that of the check plots are given for all irrigations.

## TABLE 12

*Improvement in water infiltration in treated plots over a period of years, as shown by differences between means of measurements (treated plots minus check plots)*

5-hour distance, in feet

| PERIOD | TRACTOR-COMPACTED | | DISKED | |
|---|---|---|---|---|
| | Plot 2 (dry) | Plot 6 (wet) | Plot 3 (dry) | Plot 7 (wet) |
| | ft. | ft. | ft. | ft. |
| First 3 years (1935, 1936, and 1937) | 61 | 112 | 60 | 44 |
| Final 3 years (1940, 1941, and 1943) | 8 | 45 | 23 | 10 |

The second notable variation is to be found in the differences between check plots and treatment plots. In order to ascertain the long-range trend in water

infiltration for the treated plots, in contrast to that of the check plots, and to reduce the annual fluctuations noted above, the mean values, for each irrigation, of the 5-hour distances per furrow of the three check plots were subtracted from those of the treated plots and the differences plotted as shown in figure 9. The greater the values on the ordinate, the poorer is the water infiltration relative to that of the checks. In table 12 the mean increase in 5-hour distances for treated plots over check plots is presented for the first and final 3-year periods.

In figure 9 and table 12, attention should first be directed to the prior measurements made on plot 7, which was disked while wet. In contrast to the almost normal water penetration noted in the first irrigation after the soil manipulation, subsequent observations, made during irrigations of soil which had dried thor-
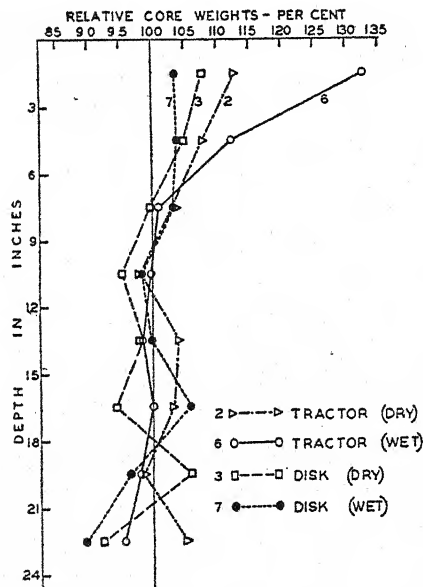


FIG. 10. CORE WEIGHTS OF TREATED PLOTS, RELATIVE TO THOSE OF CHECK PLOTS, IN 1935, IN PERCENTAGE OF SIMILAR RATIOS IN 1943

Values greater than 100 per cent indicate decreases in core weight during the period.

oughly, indicated a pronounced, adverse effect of this treatment on water penetration. This practice, like that used in the other treatments, must therefore be regarded as definitely harmful.

From both figure 9 and table 12, it may be clearly seen that with advancing years all treated plots showed great improvement in water penetration in relation to check plots. The plot disked in a wet condition (no. 7) and the plot worked with the tractor while in a dry condition (no. 2) nearly recovered their original rates of water infiltration by 1940. The soil that was compacted with the tractor while wet (plot 6) remained relatively the poorest in 1943, but its improvement was very marked. The soil disked while dry (plot 3) also improved, but perhaps not to the same point as that disked while wet or that dry-compacted by the tractor.

During the period of observation, the growth of mustard and of weeds gradually improved in the treated plots. In the winter of 1943–44, the growth was virtually equal on all plots, as shown in figure 8 for the wet-compacted plot (no. 6) and the adjacent check plot.

In July, 1943, resistance values and core weights were determined in a manner comparable to that used in 1935. Certain definite changes were clearly observable. The resistance values of treated plots, relative to those of check plots, decreased markedly in the upper soil layers (0 to 9 inches) of plots 2 and 3. Plot 6, treated with the tractor when wet, showed by far the greatest reduction in resistance values for the surface soil. In plot 7, however, which was disked while wet, the first two horizons indicated more compaction in 1943 than in August, 1935. It is very probable that the increased resistance in plot 7 occurred in the fall of 1935 as a result of the first thorough drying out of the soil after its manipulation. This assumption is in accord with the reduction in water penetration observed in the irrigation of November, 1935.

The changes in core weight from 1935 to 1943, for the compaction plots, are shown in figure 10. The depth of the soil is plotted on the vertical axis, and the change in core weight, on the horizontal axis. The mean values plotted are the core weights of the treated plots in 1935, relative to those of the check plots in 1935, expressed as percentages of similar data for 1943. The values on the horizontal axis were therefore calculated as follows, mean values of three check plots being used:

$$\frac{\text{Treated plot, 1935}}{\text{Check plots, 1935}} \div \frac{\text{Treated plot, 1943}}{\text{Check plots, 1943}} \times 100$$

Values greater than 100 per cent denote a greater core weight in 1935 than in 1943. For the check plots (nos. 1, 4, and 5) the mean core weights in those years are as follows:

| Soil depth, in inches | Core weight (grams per cubic centimeter) | |
|---|---|---|
| | 1935 | 1943 |
| 0– 3 | 1.14 | 1.41 |
| 3– 6 | 1.32 | 1.50 |
| 6– 9 | 1.46 | 1.55 |
| 9–12 | 1.36 | 1.39 |
| 12–15 | 1.42 | 1.39 |
| 15–18 | 1.41 | 1.39 |
| 18–21 | 1.31 | 1.36 |
| 21–24 | 1.42 | 1.35 |

According to figure 10, the relative core weights of the lower horizons (below 9 inches) cluster about the 100 per cent line, indicating that within the limits of variability no relative change has taken place in any of the treated plots. On the other hand, the relative core weights of the surface soils reveal that the soils of the treated plots were less compact, relative to the checks, in 1943 than in 1935.

The observations embodied in figures 9 and 10 are in harmony with the hypothesis that reduction of cultivation will improve the structure of overcultivated and compacted soil, and thus improve its water-infiltration capacity.

## SUMMARY

Rates of infiltration of irrigation water into Ramona loam soil of an experimental orchard of the University of California Citrus Experiment Station, Riverside, California, were found to vary widely according to fertilizer treatments. Incorporation of organic matter as cover crop or manure greatly increased the rate of water infiltration over that of plots which received only urea as a fertilizer. The improvement was related to the quantity of organic matter applied. Winter cover crops were slightly superior to dairy manure applied in amounts to supply 1 pound of nitrogen per tree annually.

The differences in water penetration are corroborated by differences in resistance values (the energy, in foot-pounds per inch, required to force the sampling tube into the soil, with soil moisture at field capacity) and in core weights (apparent densities) of the soils. To a depth of 9 or 12 inches, the soils of the urea plots were heavier and more resistant than the soils of the plots receiving organic materials.

Compared with the soils of a dry-farmed area adjacent to the orange grove, the soils of the orchard are characterized by lower rates of infiltration and by greater compaction, especially at a depth of 6 to 12 inches. It is suggested that these effects are largely the result of cultivation practices and of traffic in the orchard.

The hypothesis that soil compaction is influenced by traffic and cultivation was tested by subjecting both dry and wet plots of the dry-farmed area to intensive traffic by a track-type tractor and to repeated disking. The effects of the tractor were very detrimental to water infiltration in both dry and wet soil. In the wet soil pronounced soil compaction was produced. Disking of dry soil and of wet soil greatly reduced water infiltration and increased resistance and core-weight values, but the effect on wet soil did not occur until the second irrigation after treatment. Elimination of all cultivation on these plots, in conjunction with the growing of annual cover crops, the above-ground portions of which were removed, produced marked improvement in water penetration during a period of 8 years. Resistance values and core weights also became more normal during that period.

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# EFFECT OF POTASSIUM AND MAGNESIUM SULFATES AND CHLORIDES UPON THE FORMATION OF OXIDIZED AND REDUCED ORGANIC COMPOUNDS IN PLANTS

## A. V. VLADIMIROV

*Gedroiz Research Institute of Fertilizers, Agrotechnology, and Soil Science*

Many investigations of the physiological role of potassium have shown that a sufficient supply of this nutrient is essential for the synthesis of protein substances, for the translocation of carbohydrates (7), and for the formation of firm mechanical stalk tissues in cereal, flax, and other plants. There are indications, also, that potassium stimulates the process of assimilation in plants (2).

In the investigations carried on by physiologists and agrochemists in this country and abroad (4), sufficient light has been shed on the problems relating to the metabolism of nitrogenous compounds and carbohydrates in plants as affected by mineral nutrition. On the other hand, the metabolism of organic acids as affected by mineral nutrition (1) has not yet been very thoroughly investigated. The latest researches of this laboratory have, therefore, been concerned primarily with this problem. These investigations have established the fact that there is a pronounced difference in the metabolism of organic acids in plants, depending upon whether the plants are provided with ammonium or nitrate nutrition (8). Plants of the coarse variety of tobacco (*Nicotiana rustica*) when supplied with ammonium nitrogen showed a marked decrease in organic acid content, whereas those provided with nitrate nitrogen showed a marked increase. Analogous conclusions were reached by Vickery and others (6).

This paper sets forth the results of investigations on the effect of potassium and certain other mineral elements upon the formation of oxidized and reduced organic compounds in plants.

## EXPERIMENTAL DATA

To study the effect of potassium upon the formation and storage of organic acids in plants, *N. rustica* was grown in a number of sand cultures. The culture solutions were prepared with tap water and had a reaction of pH 6.5. The salt solutions and their concentrations, with the exception of nitrogen and potassium, were the same for all the cultures. Potassium was supplied in concentrations of 20 to 100 mgm. $K_2O$ per liter of solution, and nitrogen, as $NH_4$, $NO_2$, and $NO_3$, in concentrations of 40 and 100 mgm. After the plants were harvested, the leaves were kept in ether fumes for 30 minutes and then dried. The content of citric and malic acids was then determined. The results are presented in table 1.

These data show that as the quantity of potassium is increased, the content of organic acids (citric and malic) in tobacco leaves diminishes, but not pro-

portionately, in plants grown on a nitrate solution, whereas in plants grown on an ammonium solution the organic acid content tends to increase. If the direction of oxidation-reduction processes in plants is judged by the storage of organic acids in tobacco leaves (8), it may be said that the effect of potassium upon the oxidation-reduction processes differs with the availability of either ammonium or nitrate nutrition: *in plants grown on nitrates, which stimulate the oxidation processes, potassium tends to stimulate the reduction processes, whereas in plants grown on ammonium nitrogen, which stimulates reduction processes, potassium tends to stimulate the oxidation processes.*

The assertion made by some investigators (5) that potassium stimulates only the oxidation processes, cannot, therefore, be considered sufficiently well founded.

It is quite possible that other substances, besides potassium, contained in a mineral nutrient may, likewise, have a mutually opposite effect upon the

TABLE 1

*Citric and malic acid contents of tobacco leaves as influenced by the proportion of potassium in $NO_3$, $NO_2$, and $NH_4$ solutions*

Acid analyses on dry-weight basis

| CULTURE SOLUTION | | | CITRIC ACID | MALIC ACID |
|---|---|---|---|---|
| Form of nitrogen | Concentration per liter | | | |
| | N | K₂O | | |
| | *mgm./l.* | *mgm./l.* | *per cent* | *per cent* |
| NH₄ | 40 | 20 | 0.76 | .... |
| NH₄ | 40 | 80 | 0.81 | .... |
| NO₃ | 40 | 20 | 3.90 | .... |
| NO₃ | 40 | 80 | 2.22 | .... |
| NH₄ | 100 | 20 | 1.13 | 2.21 |
| NH₄ | 100 | 100 | 1.11 | 2.65 |
| NO₂ | 100 | 20 | 4.48 | 5.10 |
| NO₂ | 100 | 100 | 2.97 | 4.30 |
| NO₃ | 100 | 20 | 4.83 | 5.91 |
| NO₃ | 100 | 100 | 2.55 | 6.12 |

oxidation-reduction processes in plants grown on ammonium and nitrate nutrition. The grounds for this supposition are furnished by the results with potassium and also by the data obtained by Vlasuk (9) in regard to manganese.

The principles expressed above provide a new approach to the physiological evaluation of potassium for various plants when grown on either ammonium or nitrate nutrients.

In a comparative study of the effect of potassium on the formation of oxidized (organic acids) and reduced organic compounds (caoutchouc) in plants grown on either ammonium or nitrate nitrogen, an experiment on kok-saghyz was conducted simultaneously with the experiments on tobacco. The plants were set out in sand in individual crocks, and until August 10 all were provided with the same culture solution. On August 10, the plants were thoroughly washed, first with tap water and then with distilled water, to remove all traces of the

nutritive substances. They were then supplied with various culture solutions until harvested. The normal nutrient mixture was taken as a base, except that part of the $KH_2PO_4$ was replaced by $Na_2HPO_4$, and, in the ammonium series, $Ca(NO_3)_2$ was replaced by a mixture of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. The proportion of potassium was increased by the addition of potassium chloride.

Kok-saghyz differs markedly from the coarse variety of tobacco in its physiological nature. In particular, the physiological and biochemical processes in the kok-saghyz plant result in the storage of a reduced organic compound, caoutchouc, whereas those in the coarse variety of tobacco result in the storage of an oxidized product—organic acid. Obviously, then, the kok-saghyz should

TABLE 2

*Effect of increasing the proportions of potassium in ammonium and nitrate cultures on the crop yield and citric and malic acid content of N. rustica*

| CULTURE SOLUTION | | | AVERAGE WEIGHT OF FRESH LEAVES PER PLANT | TOTAL CITRIC + MALIC ACID | CITRIC + MALIC ACID CONTENT OF BLADES OF 1 PLANT |
|---|---|---|---|---|---|
| Form of nitrogen | Concentration | | | | |
| | N | K₂O | | | |
| | mgm./l. | mgm./l. | gm. | per cent | gm. |
| NO₃ | 100 | 20 | 523.9 | 10.74 | 4.08 |
| NO₃ | 100 | 100 | 497.5 | 8.67 | 3.30 |
| NH₄ | 100 | 20 | 412.1 | 3.34 | 1.03 |
| NH₄ | 100 | 100 | 433.0 | 3.76 | 1.25 |

TABLE 3

*Effect of increasing the proportions of potassium in ammonium and nitrate cultures on the crop yield of kok-saghyz and the total output of caoutchouc*

| CULTURE SOLUTION | | DRY WEIGHT OF 100 ROOTS | CAOUTCHOUC | YIELD OF CAOUTCHOUC PER 100 ROOTS |
|---|---|---|---|---|
| Form of nitrogen | Potassium per kgm. of sand | | | |
| | m.e. | gm. | per cent | gm. |
| NO₃ | 0.5 | 199.5 | 2.85 | 5.69 |
| NO₃ | 2.0 | 215.0 | 3.06 | 6.58 |
| NH₄ | 0.5 | 253.0 | 3.48 | 8.80 |
| NH₄ | 2.0 | 212.0 | 4.16 | 8.82 |

be provided with external conditions that ensure an intensification within the plant organism of the reduction processes, whereas tobacco should be provided with conditions ensuring the intensification of the oxidation processes.

The data in table 2 show that with an increase in potassium from 20 to 100 mgm. per liter of solution, the average weight of the leaves from one plant of *N. rustica* grown on nitrates decreased 26.4 gm. and the total citric and malic acid content decreased 2.07 per cent. In plants grown on ammonium nitrogen, an increase in the quantity of potassium was accompanied by a considerably higher crop yield and by a higher content of organic acids. In the experiment with kok-saghyz (table 3), increasing the potassium from 0.5 to 2.0 m.e. per

kilogram of sand for plants grown on nitrates increased the weight of 100 dry roots by 15.5 gm. and the output of caoutchouc by 0.89 gm., whereas for plants grown on ammonium nitrogen, increased potassium reduced the yield by 41 gm. and had virtually no effect on the output of caoutchouc.

The physiological effects of the components of potassium fertilizers—magnesium, sodium, and calcium chlorides and sulfates—on the formation of oxidized and reduced organic compounds in plants were studied on kok-saghyz and on a finer and a coarser variety of tobacco. Experiments with the finer variety of tobacco were conducted in 1938 on sand and with a modified culture solution patterned after Hellriegel's. There were four harvests, the tobacco leaves being collected as soon as they were ripe. After being harvested, the leaves were dried first in the greenhouse in the shade and then in a desiccator at a temperature of 40 to 45° C. Samples for analysis were made up from the upper and lower

TABLE 4

*Effect of chlorides and sulfates of K, Na, Mg, and Ca upon the yield and chemical composition of tobacco leaves*

Results on dry-weight basis

| CULTURE SOLUTION | WEIGHT OF LEAVES FROM 1 PLANT | MOIS-TURE PER 100 GM. | NITROGEN | | SUGARS | | CITRIC ACID | NICO-TINE |
|---|---|---|---|---|---|---|---|---|
| | | | Non-protein | Protein | Total | Reduc-ing | | |
| | gm. | gm. | per cent | per cent | per cent | per cent | per cent | per cent |
| Normal nutrient mixture (K)..... | 15.27 | 525 | 0.55 | 1.12 | 8.45 | 7.38 | 1.41 | 0.78 |
| K + KCl (2 m.e.)................ | 17.8 | 735 | 0.80 | 1.16 | 8.43 | 7.07 | 1.33 | 1.00 |
| K + K₂SO₄ (2 m.e.)............. | 19.4 | 519 | 0.55 | 0.94 | 13.82 | 11.03 | 1.03 | 0.91 |
| K + NaCl (2 m.e.)............. | 16.2 | 678 | 0.63 | 1.22 | 7.89 | 7.35 | 2.20 | 0.97 |
| K + Na₂SO₄ (2 m.e.)............ | 16.8 | 585 | 0.53 | 1.12 | 8.79 | 7.33 | 1.35 | 1.11 |
| K + MgCl₂ (2 m.e.)............. | 14.3 | 879 | 0.79 | 1.40 | 5.39 | 4.16 | 3.06 | 1.22 |
| K + MgSO₄ (2 m.e.)............ | 15.2 | 619 | 0.64 | 1.20 | 7.38 | 5.66 | 1.88 | 0.78 |
| K + CaCl₂ (2 m.e.)............. | 15.0 | 778 | 0.52 | 1.24 | 8.04 | 6.96 | 1.84 | 0.88 |
| K + CaSO₄ (2 m.e.)............. | 15.3 | 634 | 0.54 | 1.05 | 7.63 | 5.96 | 1.08 | 0.66 |

leaves of all the plants of each of the cultural varieties. The chemical composition of the lower leaves is given in table 4.

The results indicate that the yield of leaves is somewhat lower from tobacco plants grown on chlorides than from those grown on sulfates. It should be noted that in fresh tobacco leaves the water content is higher for chlorides than for sulfates.

Furthermore, the addition of potassium and sodium to the Hellriegel culture solution markedly increases the yield of leaves, whereas the addition of magnesium and calcium either fails to affect the yield or lowers it somewhat. This negative effect of calcium and magnesium is obvious to an even greater degree in the quality of the tobacco. As it is well known, the quality of cigarette tobacco is determined by its content of sugars and nitrogenous compounds, especially proteins; that is, the higher the sugar content and the lower the protein content, the higher is the quality of tobacco. In these experiments, the sugar content of the plants is lower and the protein nitrogen content is

higher when calcium and magnesium are added to the nutrient solution than when they are not.

It is evidently not the direct action of the chlorine, therefore, that accounts for its negative effect upon the quality of field-grown tobacco, as asserted in the literature on the subject, but its indirect action, in consequence of its activation of calcium and magnesium in the reaction that takes place between potassium chloride fertilizers (for instance 30 to 40 per cent potassium salts and sylvinite) and the adsorbing complex of the soil, which contains calcium and magnesium in relatively large quantities. The resulting increase in the concentration of calcium and magnesium chlorides in the soil solution causes calcium, magnesium, and chlorine to be stored in the tobacco leaves in relatively greater quantities, which may markedly lower the quality and particularly the fire-holding capacity of tobacco.

The data in table 4 indicate that, in comparison with sulfates, the chlorides of potassium, sodium, magnesium, and calcium are conducive to the greater storage of nonprotein and protein nitrogen and of nicotine in tobacco leaves and the lesser storage of total sugars.

It is interesting to note that although the chloride cultures contained smaller quantities of sugars, the percentage of reducing sugars in the total sugars was much higher than in the corresponding sulfate cultures.

These facts show that, in comparison with the sulfates, chlorides evidently further the hydrolysis of both nonreducing sugars and protein substances, converting the former into reducing sugars and the latter into amino acids and into base products, particularly nicotine, which is assumed to be the product of the secondary synthesis of the products obtained from the hydrolysis of protein substances. On the other hand, as may be seen from the figures in table 4, the chloride cultures contain much more citric acid than do the sulfate cultures.

These data indicate that, in comparison with the sulfates, chlorides intensify the oxidation processes in the plant, which further the storage of oxidized products such as citric acid.[1]

Comparison of the chemical analyses of the cultures shows that the lower the sugar content, the higher is the citric acid content. Evidently the greater expenditure of sugar in the chloride cultures is due to the synthesis of the nitrogenous compounds, particularly nicotine, on the one hand, and the production of organic acids, particularly citric acid, on the other. In so far as the chlorides, as compared with the sulfates, stimulate the oxidation processes in the plant organism, a higher content of citric acid might be expected in the coarse variety of tobacco as well as in the finer variety. And, indeed, the experiments with the coarse variety of tobacco grown in sand cultures have shown that the introduction of sodium chloride in addition to potassium chloride markedly increases the crop yield and the citric acid content of the leaves. A field experi-

[1] One may ask why more organic acids are stored in the nitrate cultures than in the sulfate cultures, when both nitrates and sulfates are oxidized compounds. Unfortunately these cultures cannot be compared, for in the one case $NO_3^-$ is replaced by $NH_4^+$, and in the other, $SO_4^-$ by $Cl^-$, and in both cases the concern is with the relative changes in the organic acids.

ment with coarse tobacco on the Staro-Yurevo State Tobacco Farm, Tambov Region, bears out these findings, as shown in table 5.

It was assumed that, since both the sulfate and ammonium ions stimulate the reduction processes in the plant, a combination of the two should further the storage of reduced organic compounds in plants, particularly of caoutchouc in kok-saghyz. Moreover, in laboratory studies in 1936, determinations of the oxidation-reduction potentials in the juice of sugar beet roots showed that the magnesium chloride cultures markedly stimulated the reduction processes, whereas the cultures with sodium, calcium, and potassium nitrates gave approximately the same results as those obtained with the controls (7). On the basis of these determinations it was suggested (7) that the addition of magnesium to the culture solution would lead to an intensification of the reduction processes in the plant. In laboratory experiments in 1937, Mosolov (3) established the fact that magnesium greatly increased the fat content of sunflower seeds, which

TABLE 5

*Effect of NaCl on crop yield and quality of coarse tobacco*

Analyses on dry-weight basis

| CULTURE SOLUTION | AVERAGE YIELD OF FRESH TISSUE PER 50-SQ.M. PLOT | CITRIC ACID | NICOTINE | SUGAR | | NITROGEN | |
|---|---|---|---|---|---|---|---|
| | | | | Total | Reducing | Protein | Nonprotein |
| | kgm. | per cent | per cent | per cent | per cent | per cent | per cent |
| NPK.......................... | 52.3 | 2.95 | 11.66 | 4.78 | 2.64 | 2.15 | 2.32 |
| NPK + NaCl................. | 55.8 | 4.26 | 10.19 | 5.31 | 3.39 | 2.32 | 2.02 |
| NP + sylvinite............... | 65.5 | 3.66 | 11.11 | 5.31 | 2.08 | 2.38 | 2.35 |

is evidently likewise connected with the stimulation of the reduction processes in plants.

It thus seemed that the choice of suitable fertilizers containing elements that stimulate the reduction processes in the plant, such as ammonium sulfate and magnesium chloride, could bring about a marked improvement in the quality of the roots of kok-saghyz, raising their content of the reduced product—caoutchouc. To verify this assumption an experiment was performed with kok-saghyz grown in sand cultures according to the procedure described above. Data on the crop yield and caoutchouc content of the roots are presented in table 6.

Comparison of the plants in this experiment leads to the following conclusions:

As compared with nitrate nitrogen, ammonium nitrogen tends to raise the percentage of caoutchouc in the roots of kok-saghyz and to increase the total quantity obtained from 100 roots.

Chlorides, in comparison with sulfates, reduce the caoutchouc content of kok-saghyz roots.

Of the tested cations, potassium, sodium, and magnesium, magnesium is the most favorable to the storage of caoutchouc in kok-saghyz roots.

It would seem, then, that by the use of a combination of ammonium nitrogen with potassium and magnesium sulfates, a pronounced increase could be brought about in the contents of other reduced products in plants, particularly of essential oils in essential-oil plants and of pyrethrine in the Dalmatian daisy, whereas the addition of nitrate nitrogen to potassium fertilizers containing chlorides would bring about an increase in valuable organic acids other than citric and malic, especially ascorbic acid (vitamin C). This circumstance may be of importance in fertilizing vegetables, fruit, and berries, for one of the most important factors determining the quality of these products is their content of organic acids, particularly ascorbic.

## TABLE 6

*Effect of various forms of potassium fertilizer on crop yield and quality of kok-saghyz*

| CULTURES* | WEIGHT OF 100 FRESH ROOTS | CAOUTCHOUC | YIELD OF CAOUTCHOUC PER 100 ROOTS |
|---|---|---|---|
| | *gm.* | *per cent†* | *gm.* |
| $NaNO_3$ + KCl (½ m.e.)................. | 775.0 | 2.85 | 5.69 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + KCl (½ m.e.).. | 1033.0 | 3.48 | 8.80 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + KCl (2 m.e.).. | 847.0 | 4.16 | 8.82 |
| $(NH_4)_2SO_4$ + $(NH_3)_2CO_3$ + $K_2SO_4$ (2 m.e.) | 846.0 | 5.34 | 12.12 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + $MgCl_2$ (2 m.e.) | 917.0 | 5.91 | 13.12 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + $MgSO_4$ (2 m.e.)................. | 788.0 | 8.48 | 16.45 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + NaCl (2 m.e.). | 684.0 | 5.06 | 8.20 |
| $(NH_4)_2SO_4$ + $(NH_4)_2CO_3$ + $Na_2SO_4$ (2 m.e.)................. | 1252.0 | 5.23 | 17.47 |

\* From the time of planting until August 10, all the plants were grown on the same nutrient; from August 10 to harvest, they were grown on the nutrient cultures listed.

† Of dry tissue in 100 roots.

### SUMMARY AND CONCLUSIONS

1. It has been established that potassium has a diametrically opposite physiological effect upon the metabolism of organic acids in plants grown on ammonium nitrogen as compared with those grown on nitrate nitrogen. When the concentration of potassium is increased, the content of organic acids in plants grown on nitrate nitrogen falls; whereas in plants grown on ammonium nitrogen the content of organic acids tends to increase.

Apparently, in those cases in which the oxidation processes taking place in the plant are stimulated as a result of nitrate nitrition, potassium stimulates the reduction processes, whereas in those cases in which the reduction processes are stimulated as a result of ammonium nutrition, potassium stimulates the oxidation processes.

2. The quantity of potassium provided to a plant grown on either ammonium or nitrate nitrogen should differ in accordance with the physiological nature of the plant. For kok-saghyz, for example, in which the economically valuable element is the reduced product caoutchouc, potassium concentration should

be higher and should be combined with nitrate nutrition, whereas such plants as the coarse variety of tobacco, in which the economically valuable products are its organic acids, exhibit a relatively high requirement for potassium when grown on ammonium nitrogen.

3. In all the experiments, the content of citric acid in tobacco leaves has been considerably higher for those plants provided with chloride nutrition than for those provided with sulfate nutrition. This adds weight to the assumption that, as compared with sulfates, chlorides stimulate the oxidation processes in the plant organism.

4. In contrast to the sulfates, the chlorides of potassium, sodium, magnesium, and calcium, while raising the contents of citric acid and nitrogenous organic compounds in tobacco leaves and lowering the content of sugars, thereby also lower the quality of the tobacco.

5. Whether in the form of chlorides or in the form of sulfates, calcium and magnesium have a negative effect upon the quality of tobacco grown on sand cultures. From this it is reasoned that the negative effect of potassium chloride or sylvinite as compared with potassium sulfate upon field plants is evidently not so much due to the chlorine itself, as to the calcium and magnesium chlorides, which are stored in the plant as a result of the chemical reaction that takes place between the applied potassium chloride and the adsorbed calcium and magnesium in the soil.

6. Chlorides have a positive effect upon the yield of the coarse variety of tobacco and raise the content of citric acid in its leaves.

7. Greenhouse experiments showed that the percentage and the yield of caoutchouc in the roots of kok-saghyz are higher in plants grown on sulfates than on those grown on chlorides.

8. A comparison of the effects of potassium, sodium, and magnesium upon the storage of caoutchouc showed that magnesium brings about a pronounced stimulation of the reduction processes in the plant.

9. By the choice of suitable nitrogenous and potassium fertilizers it appears possible to direct the biochemical processes in the plant toward increasing the crop yield and improving its quality by stimulating the reduction processes in some plants, when a high content of reduced products is desirable, and stimulating the oxidation processes in others, when a high content of oxidized products is desirable.

10. It is assumed that the use of ammonium salts together with potassium and magnesium sulfates would increase not only the caoutchouc content of kok-saghyz but also the content of other reduced products in plants, particularly volatile oils in essential-oil plants and pyrethrine in the Dalmatian daisy. On the other hand, the use of nitrate nitrogen together with potassium and sodium chlorides should increase the content not only of citric and malic acids but also of other valuable organic acids, particularly ascorbic acid (vitamin C). The latter hypothesis may prove of significance in the choice of nitrogenous and potassium fertilizers to be used for the cultivation of vegetables, fruit, and berries.

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# SOIL AGGREGATION AND ONION YIELDS[1]

JOSEPH RYNASIEWICZ

*Rhode Island Agricultural Experiment Station*

The effect of soil aggregation on tilth and erodibility of soil, and the factors influencing aggregation have been reported previously (2, pp. 1–9, 125–192; 16). The nature of the crop or crop rotation is known to affect soil aggregation considerably, and the object of this paper is to add to the knowledge of the effect of aggregation on crop growth. Work at the Rhode Island Agricultural Experiment Station (5, 6, 7, 8, 12, 13) has shown that some crops are deleterious and others are beneficial to certain succeeding crops. These reactions were attributed partly to the effects of soil acidity and other factors, but no single factor seemed to cause the differences noted.

Farnsworth (4) reported that sugar beet yields in Ohio were higher when the noncapillary pore space of the soil was increased, and cited substantiating evidence of other workers. Baver (2) presented data of Doiarenko which indicate that changes in the amount of noncapillary prosity, in air and water content, and in nitrate formation were most affected by the soil aggregates larger than 0.5 mm.

This work correlates onion yields with water-stable soil aggregates >0.5 mm. in diameter as determined in the laboratory, and emphasizes the need for grass cover crops to maintain or improve soil structure.

## METHODS AND MATERIALS

Samples were taken from Bridgehampton very fine sandy loam, of which the parent material is granite gneiss and other crystalline rock. This soil is used almost exclusively for potato growing in Rhode Island.

The results reported are from two different crop sequence studies.[2] Samples were taken in May and November, 1943, from the surface (0–4-inch) and subsurface (4–8-inch) layers of soil in 1/1000-acre cement frames. The soil had been placed in the frames by profile layers to a depth of about 2 feet in 1933. Four different crop rotations had been in effect for 10 years in these frames, and each treatment was in triplicate. The 3-year rotations were as follows: onions, 2 years mangels; onions, 2 years buckwheat; onions, 2 years corn; onions, 2 years redtop. The onions were early globe varieties grown from seed. For the first 3 years, mangels were grown in place of onions. The rotations were cultivated uniformly, and each year received nitrate of soda, sulfate of ammonia, superphosphate, and muriate of potash equvalent to a ton of 4-5-5 fertilizer

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[1] Contribution No. 673 of the Rhode Island Agricultural Experiment Station, Kingston, Rhode Island.

[2] The field work was planned and supervised by T. E. Odland. Laboratory studies of the 5-year rotation on field plots were made by E. A. Perry, and those with the frame soils were begun by C. H. Moran, who obtained the first set of samples. The laboratory work was supervised by John B. Smith.

per acre. The soil was limed to pH 5.4 to spading depth. Onions and mangels would have benefited from more lime, but previous trials have shown that the effects of preceding crops on those that follow are accentuated at low pH conditions. A sample of similar soil under permanent sod adjacent to the frames was taken to represent an optimum state of aggregation.

In 1939 samples were taken from two 5-year corn-potato-hay rotations (11) established in 1892 on $\frac{2}{15}$-acre field plats of the same soil type. Each rotation included 3 years of hay: one rotation with alfalfa, alsike and red clover, timothy, and redtop; and the other, without legumes. These rotations received the same cultivation and essentially the same fertilizers except nitrogen, which was applied in smaller amounts to the leguminous hay. The rotation plats were not replicated, but each plat was sampled in the spring and fall in six places to a depth of 6 to 8 inches.

For the onion rotations, sampling was done with a steel tube 4 inches long and 4 inches in diameter. To avoid compression of the soil the driven end of the tube was beveled (17, 18). The sampler was forced into the soil and withdrawn, and its contents were slipped into a quart cardboard container. To obtain the subsurface sample, it was necessary to remove the topsoil outside the sampler. For the corn-potato-hay rotations, a sampling tube 12 inches long and $2\frac{3}{4}$ inches in diameter was used.

The soils were air-dried and passed through a $\frac{5}{16}$-inch screen, the large lumps being broken up by rubbing with the fingers, and the gravel and other material left on the seive were discarded. The samples were analyzed for water-stable aggregates according to the method described by Yoder (18) except that the material <0.1 mm. was determined by the pipette technique (14). The triplicate soils from the onion rotations were composited and analyzed for carbon by the dry combustion method (9, 668–671). Organic matter was calculated by multiplying carbon by 1.724. Mechanical analysis of a composite sample representative of both frames and plats was made after dispersion with sodium oxalate.

The material of various size classes was reported as "aggregates," although unaggregated particles were included in these fractions. The percentage of true aggregates in the frames may be approximated by correcting for the dispersed material, which is assumed to be constant for all samples, since the soil was mixed by horizons before being placed in the frames. The plats were on a similar soil on an adjacent area, and mechanical analyses made previously are similar to those found for the composite sample. In all cases, however, the data for aggregates include organic matter, which was destroyed before dispersion of the mineral fraction.

## EXPERIMENTAL RESULTS

### Effect of depth and time of sampling on aggregation

Data in table 1 show the effect of depth and time of sampling on aggregates >0.5 mm. The aggregation percentages of soils in the various rotations were

averaged to give single values for a comparison of these factors. The difference between any pair of these averages should be not less than 2.5 per cent to be significant.

In all but two cases, the 4–8-inch sections had more aggregates than the 0–4-inch segments of the spring sampling. In nearly all instances, the opposite seemed to be true for a comparison of the upper and lower portions of the fall sampling, but analysis of variance (15, pp. 14–16) showed that the trend in the 0–4- and 4–8-inch sections of the fall samples was not significant.

TABLE 1

*Comparison of aggregation of soils under crops in different rotations in spring and fall, and the effect of depth on aggregation*

| CROP ROTATION | | | AVERAGE AGGREGATION OF REPLICATES FOLLOWING THIRD YEAR CROP, AGGREGATES >0.5 MM. DIAMETER* | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | Spring | | Fall | | Spring | Fall |
| 1st year | 2nd year | 3rd year | 0–4 in. | 4–8 in. | 0–4 in. | 4–8 in. | 0–8 in.† | 0–8 in.† |
| | | | per cent | per cent | per cent | per cent | per cent | per cent |
| Mangels | Mangels | Onions | 20.4 | 24.4 | 20.8 | 20.0 | 22.4 | 20.4 |
| Buckwheat | Buckwheat | Onions | 21.4 | 23.0 | 23.9 | 20.7 | 22.2 | 22.3 |
| Corn | Corn | Onions | 22.5 | 24.2 | 26.0 | 23.2 | 23.4 | 24.6 |
| Redtop | Redtop | Onions | 28.4 | 37.8 | 36.2 | 37.2 | 33.1 | 36.7 |
| Mangels | Onions | Mangels | 23.9 | 21.3 | 22.7 | 21.1 | 22.6 | 21.9 |
| Buckwheat | Onions | Buckwheat | 23.3 | 24.7 | 24.5 | 21.8 | 24.0 | 23.2 |
| Corn | Onions | Corn | 25.2 | 24.1 | 27.0 | 26.2 | 24.7 | 26.6 |
| Redtop | Onions | Redtop | 31.6 | 36.1 | 36.0 | 35.3 | 33.9 | 35.7 |
| Onions | Mangels | Mangels | 21.9 | 25.4 | 21.4 | 21.8 | 23.7 | 21.6 |
| Onions | Buckwheat | Buckwheat | 21.6 | 25.9 | 26.4 | 22.5 | 23.8 | 24.5 |
| Onions | Corn | Corn | 26.3 | 30.6 | 25.9 | 25.7 | 28.5 | 25.8 |
| Onions | Redtop | Redtop | 35.6 | 46.8 | 41.4 | 37.4 | 41.2 | 39.4 |
| | | Average‡ | 25.2 | 28.7 | 27.7 | 26.1 | 27.0 | 26.9 |

\* After chemical dispersion, a composite sample (0–8 inches) had 14.8 per cent mineral material >0.5 mm., and 67.0 per cent of material <0.05 mm.

† Averages for 0–4 plus 4–8-inch samples.

‡ 2.5 per cent is the least difference for significance between averages.

When the aggregation values for the surface plus the subsurface soils were averaged, no consistent treand was noted between the spring and the fall results. The top portions of the fall samples were significantly better aggregated, however, than the corresponding parts of the spring samples. This was accentuated for the redtop-redtop-onions rotation.

### Effect of crops and crops rotations on aggregation

The effect of the individual crops in four different onion rotations is shown in table 2. The results indicate that aggregation following onions was consistently

lower than that after any other crop in the rotations studied. Assuming that the soil structure under permanent sod was in an optimum condition, the effect of onions was especially marked where good aggregation once existed. This may be noted in the case of onions following 2 years of redtop, particularly in the spring sampling.

Redtop had a remarkable effect in building soil aggregates, and 2 years of this grass left the soil more highly aggregated than 1 year of the crop. Corn and buckwheat were slightly more effective in building aggregates than were mangels.

TABLE 2

*Effect of different crops and crop rotations on soil aggregation*

| CROP ROTATION | | | AVERAGE AGGREGATION OF REPLICATES FOLLOWING THIRD YEAR CROP, AGGREGATES >0.5 MM. DIAMETER | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1st year | 2nd year | 3rd year | Spring 0–4 in. | Fall 0–4 in. | Average for entire rotation | Spring 0–8 in. | Fall 0–8 in. | Average for entire rotation |
| | | | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Mangels | Mangels | Onions | 20.4 | 20.8 | | 22.4 | 20.4 | |
| Mangels | Onions | Mangels | 23.9 | 22.7 | 21.8 | 22.6 | 21.9 | 22.1 |
| Onions | Mangels | Mangels | 21.9 | 21.4 | | 23.7 | 21.6 | |
| Buckwheat | Buckwheat | Onions | 21.4 | 23.9 | | 22.2 | 22.3 | |
| Buckwheat | Onions | Buckwheat | 23.3 | 24.5 | 23.5 | 24.0 | 23.2 | 23.3 |
| Onions | Buckwheat | Buckwheat | 21.6 | 26.4 | | 23.8 | 24.5 | |
| Corn | Corn | Onions | 22.5 | 26.0 | | 23.4 | 24.6 | |
| Corn | Onions | Corn | 25.2 | 27.0 | 25.5 | 24.7 | 26.6 | 25.6 |
| Onions | Corn | Corn | 26.3 | 25.9 | | 28.5 | 25.8 | |
| Redtop | Redtop | Onions | 28.4 | 36.2 | | 33.1 | 36.7 | |
| Redtop | Onions | Redtop | 31.6 | 36.0 | 34.9 | 33.9 | 35.7 | 36.7 |
| Onions | Redtop | Redtop | 35.6 | 41.4 | | 41.2 | 39.4 | |
| Permanent sod | | | | 65.3 | | | 62.8 | |

The effect of a crop on soil structure was reflected in the average aggregation of the entire rotation. The increases in aggregation caused by 2 years of the different crops in rotation with 1 year of onions were: redtop > corn > buckwheat > mangles.

### Effect of organic matter on aggregation

Average results for all of the determinations for a particular rotation (table 4) show that the redtop rotation was highest in organic matter, followed in decreasing order by the buckwheat, corn, and mangels rotations. The soil under permanent sod was highest in organic matter. A statistical analysis (10, p. 97) was made of the organic matter results and the corresponding aggregation values. The results are listed as correlation coefficients in table 3. In every case except for the spring surface samples, there was a high positive

correlation between organic matter and aggregation. For the 0–4-inch and 4–8-inch fall samples, the correlation was nearly perfect. The coefficient for the 0–4-inch spring soils was significantly lower, indicating that other factors may have influenced aggregation.

### Onion yields and aggregation

The relation of onion yields to aggregation and soil organic matter is shown in table 4. The values for organic matter, water-stable aggregates, and crop

TABLE 3

*Positive correlation coefficients for soil organic matter and water-stable soil aggregates >0.5 mm.*

| TIME OF SAMPLING | DEPTH OF SAMPLING | |
|---|---|---|
| | 0–4 inches | 4–8 inches |
| Spring and fall............................... | 0.740 | 0.857 |
| Spring...................................... | 0.606 | 0.824 |
| Fall........................................ | 0.998 | 0.899 |

TABLE 4

*Correlation of onion yields with water-stable soil aggregates and soil organic matter*

| CROP ROTATION | | | AVERAGES FOR ENTIRE ROTATION IN 1943 | | | | | | ACRE YIELDS OF ONIONS | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Spring and Fall (0–8 in.) | | | Fall (0–4 in.) | | | | |
| 1st year | 2nd year | 3rd year | Organic matter* | Aggregates >0.5 mm. | Relative state of aggregation† | Organic matter | Aggregates >0.5 mm. | Relative state of aggregation | 1937–1942 | 1910‡ |
| | | | *per cent* | *per cent* | | *per cent* | *per cent* | | *bu.* | *bu.* |
| Onions | Mangels | Mangels | 4.436 | 22.1 | 15 | 4.442 | 21.6 | 13 | 157 | 72 |
| Onions | Buckwheat | Buckwheat | 4.539 | 23.3 | 17 | 4.559§ | 24.9§ | 19 | 218 | 112 |
| Onions | Corn | Corn | 4.502 | 25.6 | 22 | 4.564§ | 26.3§ | 22 | 249 | 286 |
| Onions | Redtop | Redtop | 4.809 | 36.7 | 45 | 4.775 | 37.9 | 45 | 487 | 524 |
| | Permanent sod | | | | 100 | 7.226 | 65.3 | 100 | | |

\* Calculated on oven-dried basis. Determinations made by G. M. Owens.

† Soil under permanent sod selected as "optimum aggregation." "State of aggregation" is the difference between percentages of aggregates and of dispersed material greater than 0.5 mm. in diameter.

‡ Data published by Hartwell and Damon (5) from an experiment on similar soil.

§ Differences between these values are not significant.

yields were analyzed statistically (15, pp. 14–16). All differences were significant except those values for organic matter, aggregation, and crop yields in the onion-buckwheat-buckwheat rotation compared with corresponding values for the onion-corn-corn rotation. Since the spring samples were taken from the soil prior to preparation of the seedbed, the values for these soils may not accurately represent the amount of aggregation at planting time. The data for the fall 0–4-inch samples, however, measure the soil aggregates following onions. It was pointed out that very little difference existed between the fall

and the spring 0–8-inch samples. Assuming that spading of the soil did not change the quantity of aggregates, average values for the two samplings are listed to approximate the extent of soil aggregation during the growing season. It must be emphasized that the order of aggregation values in the different rotations was always the same regardless of the depth or time of sampling.

Table 4 shows that onion yields increased directly with the quantity of water-stable soil aggregates at both depths and sampling periods, and with soil organic matter. The aggregation value calculated as "state of aggregation" was defined by Baver and Rhoades (1) as the difference between the aggregated and the dispersed material within certain size limits. Material >0.5 mm. diameter was used for the calculations in this paper. The optimum state of aggregation of soil under permanent sod was set arbitrarily at 100 as a basis for calculating relative values for the rotations.

The onion yields in the different rotations are averages for the years 1937–1942. The entire crop for 1943 was damaged by wandering cows, and replicate yields for the 1944 crop were unsatisfactory because of a severe drought and a poor stand of onions. The yields from similar rotations on $\frac{2}{15}$-acre plats in 1910 on the same soil type substantiated the results from the cement frames (6). It might be argued that the aggregation data for 1943 are not typical for other years and therefore should not be correlated with onion yields for the preceding 6 years when aggregation was not measured. It is believed, however, that despite any yearly variation in aggregation, the quantity of soil aggregates under the different rotations will be in the same order as presented here. A positive correlation coefficient of 0.996 was found for state of aggregation and onion yields.

### Leguminous and nonleguminous hay crops and aggregation

Data for water-stable soil aggregates in the 5-year rotation of corn, potatoes, followed by 3 years of hay, with and without legumes, are listed in table 5. Both types of hay crops were very effective in building soil aggregates after potatoes. The fall samplings for both rotations show that aggregation under the individual crops increased in the following order: potatoes, 1 year hay, 2 years hay, 3 years hay. In the spring sampling of both rotations, no significant difference existed in the aggregates >0.5 mm. after 1 year, 2 years, or 3 years of hay. The hay crops, however, left the soil in a more aggregated condition than did potatoes. No results were available for aggregation of the spring soils following the corn crop because of early preparation for potatoes, but the fall samples showed considerable losses during the corn year. In both rotations, aggregation of the fall samples was greater than for the corresponding spring samples, except in one instance. The leguminous hay crops built up the soil aggregates to a greater degree than did the nonleguminous hay crops under fall conditions. In the spring, however, aggregation was greater under nonleguminous hay.

Table 6 shows the effect of six different crop rotations on waterstable aggregates in Bridghampton very fine sandy loam. Although the various rotations are not strictly comparable because of different sampling dates, aggregation

was best where 3 years of hay was included, and least where only tuberous or bulbous crops were grown.

Soil aggregates of nine different size classes were measured, and calculations indicate that the aggregates >0.5 mm. were formed from particles <0.05 mm.

## TABLE 5

*Summary\* of water-stable soil aggregates under crops in a corn-potato-hay rotation, with and without legumes*

| PRECEDING CROP | AVERAGE† OF AGGREGATES >0.5 MM. DIAMETER | | | |
| | Rotation "E"—with legumes | | Rotation "F"—without legumes | |
| | Spring sampling | Fall sampling | Spring sampling | Fall sampling |
| --- | --- | --- | --- | --- |
| | *per cent* | *per cent* | *per cent* | *per cent* |
| Corn................................ | .... | 58.9 | .... | 57.8 |
| Potatoes........................... | 40.9 | 53.4 | 44.6 | 47.9 |
| 1st year hay....................... | 51.6 | 52.4 | 56.5 | 50.7 |
| 2nd year hay....................... | 52.8 | 62.1 | 55.3 | 59.4 |
| 3rd year hay....................... | 52.6 | 64.8 | 58.6 | 60.9 |

\* From unpublished data of E. A. Perry, Rhode Island Agricultural Experiment Station.
† Average of 6 to 8 samples taken from each plat.

## TABLE 6

*Effect of different crop rotations on water-stable soil aggregates in Bridgehampton very fine sandy loam*

| CROP ROTATION | AVERAGE\* OF AGGREGATES >0.5 MM. DIAMETER | RELATIVE STATE OF AGGREGATION† |
| --- | --- | --- |
| | *per cent* | |
| 1 year onions, 2 years mangels..................... | 22.1 | 15 |
| 1 year onions, 2 years buckwheat.................. | 22.3 | 17 |
| 1 year onions, 2 years corn ...................... | 25.6 | 22 |
| 1 year onions, 2 years redtop..................... | 36.7 | 45 |
| 1 year corn, 1 year potatoes, 3 years leguminous hay.............................................. | 54.4 | 81 |
| 1 year corn, 1 year potatoes, 3 years nonleguminous hay.............................................. | 54.6 | 82 |
| Permanent sod.................................... | 62.8 | 100 |

\* Average of entire rotation calculated from aggregation following individual crops, spring and fall (0 to 8 inches).
† Permanent sod selected as optimum aggregation and rated as 100. "State of aggregation" is the difference between aggregates and dispersed particles greater than 0.5 mm.

## DISCUSSION

The need for grass cover crops in rotation with root crops in order to maintain a high state of aggregation is apparent. In this experiment it is difficult to separate the effect of aggregation and of other benefits from increased organic

matter on onion yields. The improved state of aggregation is believed, however, to be the more important factor, since a higher correlation was obtained for aggregation and onion yields than for aggregation and organic matter.

Since no data were available to compare rotational potatoes with those grown by continuous cropping, no correlation could be made between aggregation and potato yields. The Bridgehampton soil is cropped almost exclusively with continuously grown potatoes in Rhode Island, and the relation of yields to soil structure is especially important. It may be inferred that rotation with grass crops would be beneficial. Although aggregation under corn was better than that under 2 years of hay, it should not be concluded that a corn crop will build up the soil structure as well as hay. The high value for aggregation under corn may be attributed to the fact that this crop was grown on soil which had been aggregated by 3 years of hay.

In the onion and the potato rotations, the higher aggregation values under grass for the fall soils compared to the corresponding spring samples may be attributed to increased microbiological decomposition of organic matter to form cementing organic compounds during the summer months as well as to the extra canopy protection from dispersion by rain.

The soil under leguminous hay was slightly better aggregated in the fall and significantly less aggregated in the spring than the samples under nonleguminous hay. The work of Browning and Milam (3) suggests that these differences may be ascribed to the differential rate of organic decomposition of the two crops.

In the onion rotations the correlation coefficient for aggregation and organic matter in the surface soils of spring was low, whereas it was very high for the remaining soils. This difference may be attributed to dispersion of surface colloids by rain or to other winter climatic factors.

### SUMMARY

Analysis of water-stable aggregates were made for Bridgehampton very fine sandy loam under four different 3-year rotations, each including onions, and under two corn-potato-3-year-hay rotations.

As measured by soil material >0.5 mm. in diameter in the onion rotations, the topsoil of the spring samples was better aggregated than the subsoil. No significant difference was noted between the 0–4- and 4–8-inch soil layers in the fall. The fall surface samples were better aggregated than the 0–4-inch sections taken in both seasons.

Onions and mangels had a deleterious effect upon soil structure, whereas redtop was beneficial. Corn and buckwheat aggregated the soils slightly more than onions or mangels.

The soil under the various onion rotations, and under permanent sod, contained organic matter in the following increasing order: onions, 2 years mangels < onions, 2 years buckwheat = onions, 2 years corn < onions, 2 years redtop < permanent sod. Except in the 0–4-inch spring samples, there was a high positive correlation between organic matter and aggregation. There was a

straight-line relation between average yearly onion yields for a 6-year period and aggregation of soils sampled in the seventh year.

In the corn-potato-hay rotations, soil aggregation under leguminous hay crops was greater in the fall and less in the spring than under non-leguminous hay crops. Potatoes and corn were deleterious to the soil structure, whereas the hay crops were beneficial.

The average aggregation for soils under six different crop rotations, and under permanent sod, was in the following increasing order: onions, 2 years mangels < onions, 2 years buckwheat < onions, 2 years corn < onions, 2 years redtop < corn-potatoes-3 years leguminous hay = corn-potatoes-3 years nonleguminous hay < permanent sod.

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# DYNAMICS OF WIND EROSION: II. INITIATION OF SOIL MOVEMENT[1]

## W. S. CHEPIL[2]

*Canada Department of Agriculture*

It is recognized that two basic methods are commonly used to prevent the erosion of the soil by wind. The first of these is the reduction of wind velocity near the ground by such practices as the roughening of surface, the placement of obstructions in the path of the wind, and the retention of undecomposed organic materials above the ground. The second basic method is to increase the size of soil aggregates by various cropping and tillage practices. In the former method, the object is to reduce the velocity of the wind below that required to initiate soil movement; in the latter, it is to increase the minimum velocity required to initiate the movement. Virtually the whole program of wind erosion control is based on one outstanding consideration, namely, the dependence of all methods of prevention and control on the velocity of wind required to initiate soil movement.

Malina[3] divides the wind erosion process into three distinct phases; initiation of movement, transport, and deposition of soil. This paper deals with the first of these phases.

The study was undertaken to analyze the various factors determining the initiation of soil movement. A thorough analysis was made of the minimum velocity of wind, known as the threshold velocity, required to transport various types and sizes of soil grains. Furthermore, an analysis was made of the many conditions affecting the initiation of soil movement under field conditions.

Measurements of the threshold wind velocities were made in the open field and in the laboratory wind tunnel. Pitot tubes and a multiple alcohol manometer were used for making simultaneous readings of wind velocity at different heights above the ground. In the tunnel, measurements were made at the leeward end of a 12-foot length of thoroughly air-dry soil.

The soils used in the investigation differed widely in the size of the individual grains and in specific gravity. The specific gravity was determined by dividing the weight of a definite volume of the grains by the weight of an equal volume of the same sized grains of quartz sand and multiplying the quotient by 2.65. The quartz sand used was very uniform in composition and had a specific gravity of 2.65.

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### RESULTS OF WIND TUNNEL EXPERIMENTS

In uniformly mixed cultivated soils containing only erosive fractions, there was a range of wind velocity between the low point at which the most erosive particles could be removed and the high point at which there was a continuous movement of all the grains present in a mixture. The range of velocity varied widely in different samples, depending chiefly on the range of the particle size. The movement began on the part of a few most exposed fine grains for which the threshold velocity was the lowest, but it ceased as soon as these were dragged down to the level of other grains. Upon a slight increase of velocity, a definite movement of the most erosive grains took place but ceased as these were removed and the surface became stabilized with a bed of coarser grains. Upon a slight increase of velocity, a further movement took place and continued until the surface once again became stabilized with still coarser grains. Ultimately a velocity was reached which was just high enough to move all of the sizes present in the mixture. Then movement continued indefinitely.

Single grains or aggregates greater than 3 mm. in diameter were not moved by wind velocity of 30 miles per hour at 6-inch height. Such high surface velocities seldom occur during dust storms and thus have little practical significance. As most cultivated soils contained particles and individual aggregates ranging from very fine dust to clods as great as or greater than 50 mm. in diameter, there was no available velocity which would perpetuate the movement in a tunnel. Even at the highest velocity the movement would continue for a while and cease as soon as the surface became covered with a bed of aggregates too coarse to be moved by the wind. There was, in other words, no available velocity at which soil movement would continue indefinitely, as was the case with soils composed of smaller fractions only. In the case of cloddy soils containing a wide size range of erosive and nonerosive fractions, slight amounts would be transported even at fairly low velocities, but only until all the fractions transportable at that particular velocity were removed from the surface. The movement could be re-established with every increase in wind velocity, but in each case for only a limited time.

The results described above apply to level soil areas of limited length, such as in a wind tunnel, and denote the movement of the soil initiated only by the direct pressure of the wind against the ground. The lowest velocity required to produce a definite movement of the most erosive grains will be designated as the *minimal fluid threshold*, and that required to move the largest grains as the *maximal fluid threshold*. Bagnold[4] used the term *initial fluid threshold* for the velocity of wind required to initiate the movement of dune sand of predominant diameter, but this is to be distinguished from the minimal fluid threshold, which designates the velocity required to introduce a definite movement of the most erosive grains, rather than of the predominant size. Apart from various types of dune materials, most soils do not contain a predominant size fraction, but a wide range of different sizes for which the initial fluid threshold does not exist. From what follows, it will be observed that wind erosion control is based on pre-

[4] BAGNOLD, R. A. 1941 The Physics of Blown Sand and Desert Dunes. Methuen & Co. Ltd., London.

ventive measures designed against wind equal to, or exceeding, the minimal threshold, which is of much greater practical significance than the less definite and generally nonexistent maximal threshold.

The minimal fluid threshold velocity at 12-inch height was found to be from 0.5 to 3 miles per hour higher in the tunnel than on the same soil in a field equal to or exceeding one-quarter of a mile in length. If, however, a small stream of highly erosive grains was allowed to flow through the tunnel roof onto the windward end of the exposed soil area, the minimal threshold obtained in this manner was about equal to the minimal threshold for the same soil in the field. This critical velocity will be named the *minimal impact threshold*, which is the minimal velocity required to initiate soil movement by the impact force of the descending grains, carried in saltation, rather than by the direct pressure of the fluid against the most erosive grains resting on the ground.

It has been observed that once erosion was initiated, it was maintained by the impacts of particles moving in saltation and, except on the extreme windward edge of the eroding area, not by the direct pressure of wind against the ground. In the field, therefore, knolls, ridges, sand pockets, and highlime areas start to erode at a lower wind velocity than the rest of the field. Once erosion has started, however, it spreads fanwise to leeward and the bombarding action of the particles in saltation causes movement of the soil in other parts of the field which, under an equal wind velocity but without such bombardment, would remain at rest. The minimal threshold for the less exposed parts of the field is therefore determined by the minimal threshold for the most exposed, or the most erosive, spots and is consequently equal to the minimal impact, rather than the minimal fluid threshold velocity.

The wind of such a velocity as to initiate erosion of the soil is characterized by eddies and irregularities of movement of extremely variable velocity. The movement is in fact very complex, and except for the exceedingly thin layer at the surface there is much mixing of air molecules. The wind is thus made up of momentary currents blowing in all directions, whereas its measured velocity is usually the mean value of only the forward velocity. Because of turbulence, the transporting power of the wind is variable, and the threshold velocity depends not on the average forward velocity, but on the maximum momentary velocity of turbulent flow. Eddies are thus of greater importance in the lifting and transportation of the soil than is the average velocity of the wind.

In spite of the marked irregularity in the momentary velocity of the wind, the average velocity is of remarkable constancy for any height and given set of conditions and, as discovered by Prandtl, is governed by a definite aerodynamic law. The wind velocity $v$ at any height $z$ above the ground, over which no soil movement takes place, can be expressed in centimeter-gram-second units by:

$$v_z = 5.75 V_* \log \frac{z}{k}$$

where $V_*$ is the so-called "drag velocity" in the logarithmic law and determines the slope of the velocity distribution curve when the velocity is plotted against the

logarithm of height. $V_*$ is equal to $\dfrac{v_z}{5.75 \log \dfrac{z}{k}}$, in which $v_z$ is the velocity at height

$z$, and $k$ is a constant equal to one-thirtieth of the height of surface irregularity, at which height the wind velocity is zero; $v_z$ is also equal to $\sqrt{\dfrac{\gamma}{\rho}}$, where $\gamma$ is the surface drag in dynes per square centimeter and $\rho$ the density of air which, under the conditions of the experiment, was equal to $1.10 \times 10^{-3}$.

Figure 1 indicates typical wind velocity distribution curves over an eroding soil. It will be observed that, except for the fluid threshold, the velocity at a height of 0.5 cm. (that is, at height $k'$) is nearly constant no matter how great the drag velocity. At levels still closer to the ground the wind velocity is lowered as
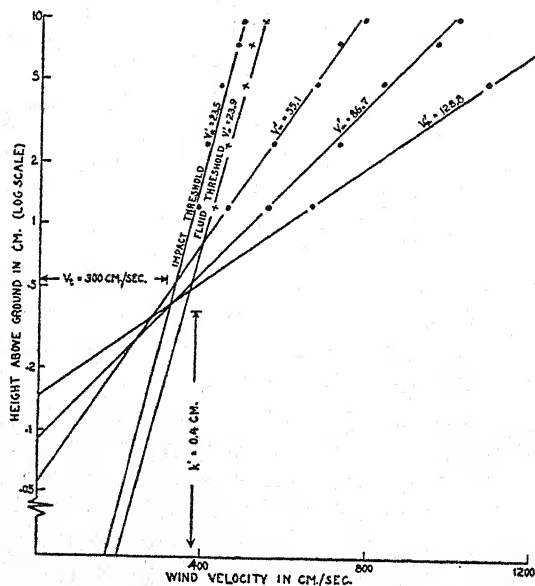


FIG. 1. WIND VELOCITY DISTRIBUTION OVER AN ERODING CLAY LOAM SOIL

the wind above becomes stronger. This has been confirmed by measurements of wind velocity in both the tunnel and the open field at very low heights above coarse soils over which the height of $k'$ generally exceeds 1 cm. In every such case an increase in wind velocity above the height $k'$ was accompanied by a corresponding decrease in velocity below this height.

As indicated in figure 1, the fluid threshold is greater than the impact threshold at all heights above the ground. The velocity at height $k'$ at the fluid threshold exceeds the constant value reached at the impact threshold. Immediately preceding the beginning of soil movement the velocity at height $k'$ rises to the fluid threshold value, but as soon as movement is initiated the drag produced by the grains in saltation immediately reduces the velocity to the lower constant value of the impact threshold. The wind velocity near the eroding surface is therefore reduced by the soil movement, and the new velocity distribution curves are

established, all with a common velocity at height $k'$. Over drifting sand, Prandtl's formula, as shown by Bagnold, becomes

$$v_z = 5.75 V'_* \log \frac{z}{k'} + V_t$$
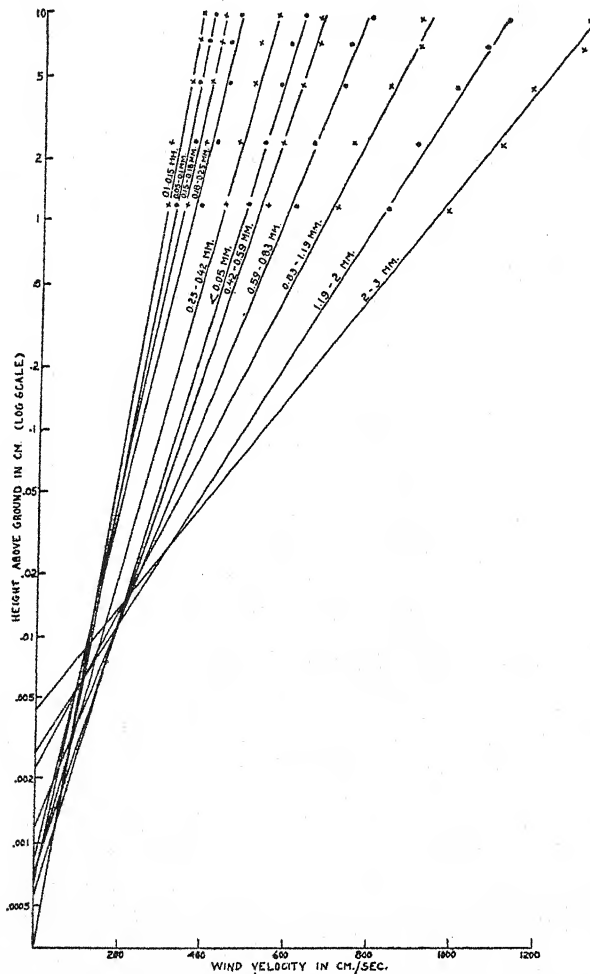


FIG. 2. MAXIMAL FLUID THRESHOLD VELOCITIES FOR CLAY LOAM GRAINS OF VARIOUS SIZES

where $V'_*$ is the new drag velocity modified by the sand movement and which is equal to $\dfrac{v_z - V_t}{5.75 \log \dfrac{z}{k'}}$, in which $V_t$ is the velocity at height $k'$, at which level the velocity remains constant at all wind speeds above that required to initiate erosion. The data obtained in these studies indicate that soil movement modifies the wind velocity in much the same way as does drifting sand, described by Bagnold.

The maximal fluid and impact threshold velocities for different sizes of clay loam grains are indicated by the data in figures 2 and 3. For very fine soil grains, of about 0.1 mm. diameter, the fluid threshold was but slightly higher than the impact threshold, but this difference is somewhat greater for the larger grains. While the ratio of fluid to impact threshold for grains of 0.1 mm. diameter was approximately 1:1.1, that for large grains of 2 to 3 mm. diameter was 1:1.13. The impact threshold for particles smaller than 0.1 mm. coincided with the fluid threshold.

The values of $V_t$ and $k'$ were determined for different sizes of soil grains for the purpose of finding any possible relationship between these values and the size
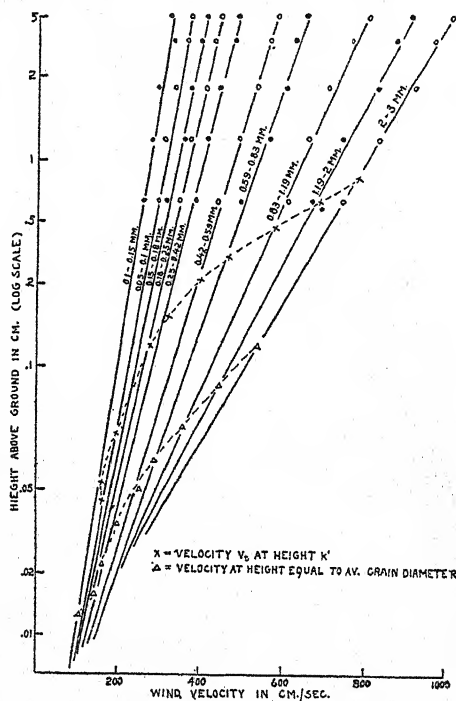


FIG. 3. MAXIMAL IMPACT THRESHOLD VELOCITIES FOR CLAY LOAM GRAINS OF DIFFERENT SIZES

of the eroding grains and surface ripples. These values were obtained by recording the wind velocity at different heights for different tunnel propeller speeds and determining the focal points to which all velocity distribution curves converged when plotted on the log-height scale. The values so determined are indicated in figure 3. To avoid superfluity the different wind velocity distribution curves converging to focal points at height $k'$ are omitted, and only the position of each point is indicated. For comparison, the velocities at heights equal to the average grain diameter, are indicated.

The data show that the magnitude of $k'$, and hence also of $V_t$, varies directly, though not proportionately, with the diameter of the eroding grains. The

height $k'$ is seen to vary with grain diameter in a ratio of 5 to 1 for very fine grains up to 0.18 mm. in diameter, 10 to 1 for grains between 0.18 and 0.7 mm., and 6 to 1 for the largest grains of 2 to 3 mm. diameter (table 1). All evidence seems to point to the conclusion that the height $k'$ is not entirely dependent on the diameter of the eroding grains, otherwise the variation would be proportionate.

The next problem was to find any possible relationship between $k'$ and the surface roughness as modified by the height and wave length of ripples commonly found on eroding soils. No matter how great the wind velocity, no ripples of measurable magnitude were formed on soils composed of particles smaller than 0.05 mm., or of particles greater than about 0.7 mm. in diameter. A definitely rippled surface was produced, however, on soils composed of intermediate-sized particles. The height and wave length of the ripples varied with different sizes

TABLE 1

*Relation of the focal point* k' *to grain diameter and size of surface ripples*

| DIAMETER OF GRAINS | RIPPLE SIZE DEPENDING ON WIND VELOCITY | | RATIO OF AVERAGE GRAIN DIAMETER TO $k'$ |
| | Height | Wave length | |
| --- | --- | --- | --- |
| *mm.* | *mm.* | *mm.* | |
| <0.05 | 0 | 0 | ... |
| 0.05–0.10 | 2 to 10 | * | 1: 5.9 |
| 0.10–0.15 | 4 to 22 | 203 to 254 | 1: 4.4 |
| 0.15–0.18 | 3 to 25 | 180 to 360 | 1: 5.3 |
| 0.18–0.25 | 3 to 15 | 150 to 285 | 1:11.0 |
| 0.25–0.42 | 2 to 10 | 142 to 275 | 1:10.6 |
| 0.42–0.59 | 0 to 4 | 100 to 255 | 1:11.0 |
| 0.59–0.83 | 0 | 0 | 1: 9.9 |
| 0.83–1.19 | 0 | 0 | 1: 8.7 |
| 1.19–2.0 | 0 | 0 | 1: 7.9 |
| 2.0 –3.0 | 0 | 0 | 1: 6.4 |

* Very irregular in wave length.

of grains and increased with wind velocity. The height $k'$, on the other hand, was not influenced by wind velocities. The increased height of ripples was expected to increase the value of $k'$ but their increased wave lengths apparently counterbalanced this tendency.

Soil surfaces composed of grains varying in diameter from about 0.1 to 0.4 mm. had the greatest tendency to become rippled under all wind velocities above that required to initiate erosion (table 1). This size is moved largely in saltation and constitutes the bulk of the material of various types of dunes. Larger sizes mainly roll and slide along the surface. In proportion to grain diameter, $k'$ is considerably lower for the larger grains, and this is evidently due to the absence of ripples and the reduced height of the saltation movement. The height $k'$ is therefore dependent on the grain diameter as well as on the type and magnitude of surface roughness.

It was found that, irrespective of the height and wave length of the ripples,

the fluid and the impact threshold velocities for any given size of eroding grains remained constant. On the other hand, they varied greatly with the diameter of the grains. The most readily eroded particles ranged from 0.1 to 0.15 mm. in diameter. Above this range of size the threshold velocity increased with the increase in size, and below this range the threshold velocity increased as the size of particles decreased. The impact threshold velocity for particles smaller than 0.05 mm. could not be determined because of great difficulty in obtaining sufficient material, but the fluid threshold velocity, requiring a much smaller sample, was determined. The threshold velocities for grains above 0.1 mm. in diameter agreed closely with the square-root law[4], namely, that the drag velocity of any fluid required barely to produce the movement of solid grains, resting on a

## TABLE 2

*Values of the coefficient A obtained for clay loam in wind tunnel experiments\**

| DIAMETER OF GRAINS | SPECIFIC GRAVITY OF GRAIN | VALUE OF $A$ | |
|---|---|---|---|
| | | At maximal fluid threshold | At maximal impact threshold |
| *mm.* | | | |
| <0.05 | 2.58 | 0.32 | 0.32 |
| 0.05–0.10 | 2.07 | 0.13 | 0.14 |
| 0.10–0.15 | 2.09 | 0.09 | 0.08 |
| 0.15–0.18 | 1.96 | 0.10 | 0.08 |
| 0.18–0.25 | 1.94 | 0.10 | 0.09 |
| 0.25–0.42 | 1.91 | 0.09 | 0.08 |
| 0.42–0.59 | 1.91 | 0.09 | 0.08 |
| 0.59–0.83 | 1.80 | 0.10 | 0.08 |
| 0.83–1.19 | 1.78 | 0.11 | 0.09 |
| 1.19–2.0 | 1.74 | 0.11 | 0.09 |
| 2.0 –3.0 | 1.65 | 0.11 | 0.08 |

\* The coefficient $A$ was calculated from the threshold velocity formula:

$$A = V_{*t} \sqrt{\frac{a - \rho}{\rho} gd}$$

level surface, varies as the square root of the product of grain diameter and the difference between the specific gravity of the fluid and the grain. Since the specific gravity of air is insignificant in comparison with the specific gravity of the soil grains, it may be disregarded for all practical purposes, and the threshold drag velocity $V_{*t}$ may therefore be assumed to vary as the square of the product of the specific gravity of the grain and its diameter. This law can be expressed by the formula:

$$V_{*t} = A \sqrt{\frac{\sigma - \rho}{\rho} gd}$$

in which $\sigma$ is the specific gravity of the grain, $\rho$ the specific gravity of the fluid, $g$ the gravity constant, $d$ the diameter of the grain in centimeters, and $A$ a coefficient the value of which in air for grains above 0.1 mm. in diameter was found

to be 0.1 for the fluid threshold and 0.085 for the impact threshold. The agreement between experimental data and the above law can be observed from table 2, in which the values of the coefficient $A$ are given for individual determinations. A perfect agreement would show a constant value of $A$. The data in figure 4 show the relationship between the threshold drag velocity, $V_{*t}$, and the product of specific gravity and diameter of the grains. The product is drawn on a square-root scale to show the relation $V_{*t} \propto \sqrt{\sigma d}$ for grains above 0.1 mm. in diameter. In view of the possible variation in the shape of the soil grains used in the experiment, the agreement is good.

For grains below 0.1 mm. in diameter the values of $A$ (table 2) rise with the decrease in grain diameter, indicating that the threshold law does not apply to
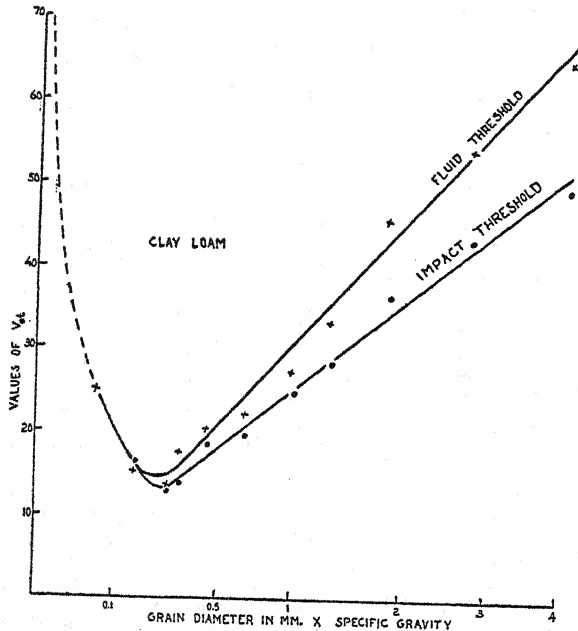


FIG. 4. VARIATION OF THE THRESHOLD VELOCITY WITH GRAIN SIZE AND SPECIFIC GRAVITY

such fine material. Because of difficulties in obtaining sufficient quantities of soil particles smaller than 0.05 mm. in diameter, it was not possible to determine accurately the values of $V_{*t}$ for such material. Small quantities of different-sized silt and very fine sand were extracted, however, from silty clay loam soil, and their relative resistance to erosion was determined by recording the maximal velocity of wind at 6-inch height required to initiate a continuous movement of particles spread in a thin layer on a 3-foot length of the tunnel floor.

The results of this experiment (table 3) show that the threshold velocity is least for particles of 0.1 to 0.15 mm. in diameter, but for particles below this size the threshold velocity increases with the decrease in the size of the grains. Fine silt particles (0.005–0.01 mm.) were very resistant to wind erosion and did not move even under a wind velocity of 37 miles per hour at 6-inch height. When

resting on a smooth glass surface, these particles required a higher wind velocity to set them in motion than if they were resting on the other similar particles in a layer of considerable thickness. Whether this increased resistance of the particles to erosion from a smooth glass surface is due to greater cohesion between the glass and the particles, or to some other cause, is not definitely known. It is evident, however, that the high resistance of the fine particles to erosion by wind is not altogether due to cohesion as might be suggested, but more particularly to the fact that the particles are too small to protrude above a laminar and more or less viscous layer of air close to the surface of the ground. Usually, the layer is so thin that the surface irregularities protrude into the turbulent, and hence more erosive, air above. It is known that the surface protrusions of the height $d$ would be within this layer as long as the Reynold's number of the form $\frac{V_* d}{\gamma}$ is less than 3.5. (Under atmospheric conditions the kinematic viscosity $\gamma$ for air can be taken as 0.14). The data obtained on clay loam soil show that the height

TABLE 3

*Maximal fluid threshold velocities for dry quartz particles\**

| SIZE OF PARTICLES | SPECIFIC GRAVITY | THRESHOLD VELOCITY | |
|---|---|---|---|
| | | Off a level layer of loose particles | Off a smooth glass surface |
| mm. | | cm./sec. | cm./sec. |
| 0.005–0.01 | 2.65 | >1,655 | >1,655 |
| 0.01 –0.02 | 2.65 | 1,060 | >1,655 |
| 0.02 –0.05 | 2.65 | 645 | 985 |
| 0.05 –0.10 | 2.65 | 412 | 390 |
| 0.10 –0.15 | 2.65 | 381 | 358 |
| 0.15 –0.25 | 2.65 | 497 | 452 |

\* Wind velocity measured at 6-inch height. Length of exposed area 3 feet.

$d$ for the most erosive grains (0.1–0.15 mm.) was approximately 0.05 mm. This size of grain apparently produced a surface roughness of approximately 0.05 mm., which was just equal to the height of the laminar layer. Grains larger than 0.05 mm. evidently were eroded more readily from a smooth surface than from a layer composed of these sizes, because of the reduced friction, as a result of slippage, along the glass surface. On the other hand, grains finer than 0.05 mm., when placed on a glass surface, were submerged in the laminar sublayer and eroded only under a relatively high velocity. But as more of these fine particle were piled in a loose layer, the surface became rougher and the threshold velocity was consequently reduced.

The high resistance of fine particles to erosion by wind is of less consequence in the field than may be expected. Particles smaller than 0.005 mm. do not exist as such in ordinary soils, for they are aggregated into larger individual grains. Single grains or aggregates 0.05 to 0.5 mm. in diameter have little or no cohesive property and are easily carried by the wind. Soil fractions that may be classed as

nonerosive, or erosive under exceedingly high winds, are silt of 0.005 to 0.05 mm. and grains larger than 1.0 mm. in diameter. No information is available on the effect of different mixtures of sand, silt, and clay particles on erosiveness. A certain proportion of clay seems to be essential for the greatest stability of the soil against the wind, but that beyond a certain limit is detrimental in some soils in that it causes the formation of small granules similar in erosiveness to dune sand.

The data presented in figure 4 show that the erosive power of wind is dependent on $V'_*$, that is, on the rate of increase of velocity with the log-height. This rate of increase of velocity, and hence of the wind drag, remains constant irrespective of whatever change may occur in the roughness of the ground surface. The threshold velocity is therefore unaffected by the surface roughness, except in that it is less distinct on a rough than a smooth surface and therefore more difficult of accurate determination. The wind drag on a rough surface is absorbed chiefly by the surface projections. Projections such as crests of ridges are therefore subject to greater erosion than the furrows, but the increase in erosion there is counterbalanced by the fact that much of the soil dislodged moves directly into the lee furrows and, if the wind is not too strong, is deposited there. This initial stage of soil movement is very limited and should not be confused with the real threshold characterized by the movement of soil from furrow to furrow along the whole length of the erosive area.

Plant material such as stubble and weeds, covering the surface of the ground usually affords protection to the whole soil surface, including clods and ridges. Depending on the extent of the cover, some or all of the drag is absorbed by this material. The threshold velocity for the plant material, even if merely scattered on the surface of the ground, is higher than for the most erosive grains; hence considerable benefit is derived from it. When the wind is strong enough to remove the plant material from the surface of the ground, the threshold velocity of the affected surface is reduced and the movement of the soil is continued under wind velocity considerably lower than before.

When vegetative matter is left anchored to the ground by the roots or by partial burial, its movement by wind is prevented. The portion below the surface offers little or no protection to the soil, but aids in the prevention of erosion by enabling the above-ground portion to withstand the greater force of wind. The development of methods to facilitate the maximum anchorage with the minimum waste of organic materials by burial is a subject of extensive investigations in Canada and the United States.

The maximum fluid threshold velocity for a range of different sizes of soil grains (table 4) was observed to be lower than that required to erode only the largest of the grains, the actual velocity depending on the magnitude of this range and the proportion of the different sizes present in a mixture. The velocity required varied directly with the average size of all of the erosive particles. The movement of the larger fractions was facilitated by impacts of the smaller grains in saltation movement, rather by direct wind pressure. The coarser material provided most of the surface creep.

The data in table 4 indicate that the movement of the difficultly erosive particles less than 0.05 mm. was facilitated by the bombarding effect of coarser fractions in saltation movement. The threshold velocity varied directly with the relative quantity of the fine material present in a mixture and inversely with the size of its particles. Once lifted off the ground, these fine dust particles remained suspended in the air and were carried slowly downward by the force of gravity only after the wind had died down.

The above results should apply in the consideration of the erosiveness of soils in the field, since it is known that these are usually composed of erosive grains of a wide range of size. Fractions that alone were not transported by wind of a definite velocity were moved freely when mixed with the more highly erosive grains, their movement being facilitated by the impacts received from the more erosive fractions.

TABLE 4

*Maximal fluid threshold velocities for different ranges of size of soil grains*

| RANGE OF GRAIN DIAMETER | VELOCITY AT 6-INCH HEIGHT | |
| :---: | :---: | :---: |
| | For the whole range of size | For only the largest grains |
| *mm.* | *cm./sec.* | *cm./sec.* |
| 0.01–0.05 | 590 | 493 |
| 0.01–0.10 | 491 | 377 |
| 0.01–0.15 | 420 | 400 |
| 0.01–0.18 | 402 | 455 |
| 0.01–0.25 | 447 | 510 |
| 0.01–0.42 | 527 | 626 |
| 0.01–0.59 | 590 | 702 |
| 0.01–0.83 | 630 | 845 |
| 0.01–1.19 | 720 | 984 |
| 0.01–2.0 | 814 | 1,251 |
| 0.01–3.0 | 1,020 | 1,474 |

### RESULTS OF MEASUREMENTS IN THE OPEN FIELD

With ordinary soils containing a certain proportion of coarse, nonerosive fractions, the movement of erosive material in the tunnel ceased as soon as the surface became protected by the coarser aggregates. Except on very restricted areas, no such cessation of movement has ever been observed in a field 40 or more rods wide. Removal of all erosive fractions from a surface of a small soil area in a wind tunnel is a matter of minutes, but removal of such fractions from large fields requires much longer periods. To remove most of the erosive fractions from a 12-foot length of exposed area, at least 30 minutes was required. On the assumption that the time required to stabilize a given area varies directly with its length, nearly 5 days of continuous exposure to erosive wind from one direction would be needed to stabilize a ½-mile length. Erosive winds, however, seldom blow continuously from one direction for such periods as this and usually die down at night. A change in wind direction would likewise prolong the period

required to stabilize a given field. Furthermore, large quantities of nonerosive soil in the field are converted to erosive material by abrasion caused by the moving soil grains, a condition not obtainable in a wind tunnel of limited length. All these factors act against complete stabilization of the soil surface in the field.

In fact, the continued action of wind on large areas of bare soil affects the ultimate erosiveness of the soil in exactly the opposite way to that in a short tunnel or a small field plot. The initiation of movement for the first time in the field commonly requires a much higher velocity than for succeeding windstorms. This is because bare fields are usually covered with a thin surface crust, which is not easily eroded and serves as a protective agent, but as soon as some particles are loosened and carried by high wind, their impacts against the surface cause abrasion on such a scale as to finally wear through the surface crust and expose the more highly erosive soil beneath. This abrasive action is most intense on the leeward side of the field where the concentration of the eroding particles is the greatest.

In addition to surface crust formation, there is still another factor influencing the threshold wind velocity of cultivated soils. Particularly in recently cultivated soils unaffected by wind erosion, there is a wide range of size of erosive and nonerosive fractions. As shown in the preceding section of this report, fine dust prevents the movement of the more erosive grains, but it is carried away in suspension faster than are the coarser grains, with the result that ultimately most of it is blown completely away and the more highly erosive grains are left near their original location in the field. As a result of attrition caused by the saltation movement, nonerosive clods become broken down to fine, highly erosive grains. Under such conditions, soil materials carried in saltation are being continually sorted out from the less erosive fractions and may, in fact, pile up into hummocks or dunes of various sizes and with irregular distribution to cover much of the originally cultivated surface. This condition is developed most rapidly on the leeward portion of the eroding area but may extend over much of the other parts as a result of the variability in the direction of the erosive winds. The susceptibility of the soil is thus increased, and the threshold velocity decreased, with each succeeding windstorm. This fact is indicated to some degree by data in table 5, which show the minimal fluid and impact threshold velocities of several freshly cultivated soils and of dune materials originating from these soils as a result of continued exposure to erosive winds. The difference in the field is often even greater than that indicated in table 5, for, though the threshold for dune materials corresponds to about the lowest possible in the field, that for the noneroded soils may be even higher than indicated, especially under weather conditions favoring the formation of a hard surface crust.

There is, therefore, a range of threshold velocity for any soil, depending on the previous history of the exposed field, and this range varies from the threshold velocity of the drifted dune material to the threshold of the previously noneroded field. This range may be anywhere from 13 to 30 miles per hour at 1-foot height. Once a bare field has been exposed to continued action of erosive winds, however,

it generally starts to erode when the wind reaches a velocity of 13 to 15 miles per hour at a 1-foot height[5].

An intervening rain may have some effect on increasing the threshold velocity, but it has been observed that such effects, if any, are generally small. What little cementation may have taken place as a result of the rain is generally not sufficient to cause an appreciable increase in the threshold velocity. This is because dune materials are devoid of the fine individual particles (< 0.02 mm.) necessary to bind the larger grains together. A few grains moving in saltation is all that is necessary to loosen the weakly cemented mass and to start it in motion with the wind.

### TABLE 5

*Minimal impact and fluid threshold velocities for various cultivated soils and for dune materials resulting from exposure of these soils to wind erosion[*]*

| SOIL TYPE | MINIMAL IMPACT THRESHOLD AT 12-INCH HEIGHT | | MINIMAL FLUID THRESHOLD AT 12-INCH HEIGHT | |
|---|---|---|---|---|
| | Cultivated soil | Dune material | Cultivated soil | Dune material |
| Regina heavy clay | 23.1 | 14.5 | 24.6 | 15.7 |
| Sceptre clay | 23.0 | 14.2 | 24.2 | 15.2 |
| Fox Valley silty clay loam | 23.0 | 13.1 | 23.9 | 13.9 |
| Cypress clay loam | 21.1 | 13.7 | 22.1 | 14.1 |
| Haverhill loam | 20.5 | 12.8 | 21.1 | 13.6 |
| Haverhill light loam | 20.4 | 13.0 | 21.7 | 13.7 |
| Hatton fine sandy loam | 18.5 | 14.3 | 19.2 | 14.9 |

* The dune materials were freshly drifted soils, still unaffected by rain, obtained from small dunes, either next to or right on the sampled cultivated fields. These samples of drifted soil represent that portion which has been moved about by the wind and deposited in mounds next to various obstructions.

### CONCLUSIONS

The minimum velocity of wind required to initiate soil movement, known as the *threshold velocity*, has been considered for various conditions of soil, roughness of surface, and size of eroding area. It has been shown that the condition of the soil in the field, and hence its threshold velocity, varies greatly from day to day. For this reason it is virtually impossible to predetermine the relative erosiveness of a field, unless the effect of all the factors affecting erosion is known. Numerous factors are often involved.

The greatest single factor influencing the threshold velocity is the size of soil grains. The threshold velocity is least for grains 0.1 to 0.15 mm. in diameter, these requiring a velocity of 8 to 9 miles per hour at 6 inches above the ground. Above this range of size the threshold velocity increases with the increase in size of grains, whereas below that it increases with the decrease in the size of particles.

[5] CHEPIL, W. S., AND MILNE, R. A. 1939 Comparative study of soil drifting in the field and in a wind tunnel. *Sci. Agr.* 19: 249–257.

For grains above 0.1 mm. the threshold velocity varies as the square root of the product of their specific gravity and diameter. The specific gravity of individual soil grains varies from about 1.65 to 2.65, but the average specific gravity for ordinary mineral soils varies much less than this, and differences in threshold velocities caused by differences in specific gravity are generally very small.

The high resistance of fine dust particles to erosion by wind appears to be due partly to cohesion but mainly to the fact that the particles are too small to protrude above a laminar and viscous layer of air close to the surface of the ground. Fine dust is lifted off the ground mainly by impacts of larger grains which are more erosive by virtue of the fact that they are larger and protrude into the fast moving, turbulent current of air higher up. Because of cohesion, the threshold velocity is lowered considerably by the presence of dust in mixtures with coarser grains.

The threshold velocity for soil grains of a range of size above 0.1 mm. is lower than that required only for the largest grains, the actual velocity varying inversely with the magnitude of this range. The movement of the largest fractions is facilitated by bombardment from smaller grains in saltation, rather than by direct wind pressure. Soil grains that are moved most easily by erosive wind range from 0.1 to 0.5 mm. in diameter. This range of size predominates in most types of dunes.

The erosive power of wind is dependent on the rate of increase of velocity with log-height. This rate of increase, and hence of the wind drag, is unaffected by any change that may occur in the roughness of the ground. The threshold velocity is therefore unaffected by surface roughness.

The threshold velocity for undecomposed crop residues and weeds, even if merely scattered on the surface of the ground, is higher than for most of the erosive grains; hence, if the wind is not too strong, some or all of the drag is absorbed by this material and erosion of the soil is reduced considerably. If, however, the wind is strong enough to remove the crop residue, the threshold velocity of the affected surface is reduced and the movement of soil will continue under wind velocity lower than before.

The same general effect occurs in fields unprotected by crop residue. The initial threshold velocity for a bare field is often much higher than for succeeding windstorms. This is due to several causes, one of which is the existence of a thin surface crust, which is not easily eroded but which under continued abrasive action on the part of some loose grains commonly becomes completely disintegrated and loses its protective value.

Another factor influencing the threshold velocity of cultivated soils is the sorting action of the wind, resulting in accumulations of dunes requiring a much lower threshold velocity than the noneroded field. The threshold velocity for dune materials is the lowest possible in the field and varies little with soil type.

There is, therefore, a range of threshold velocities for any soil, depending on the previous history of the field, and this range varies anywhere from 13 to at least 30 miles per hour at 1-foot height above a smooth ground surface.
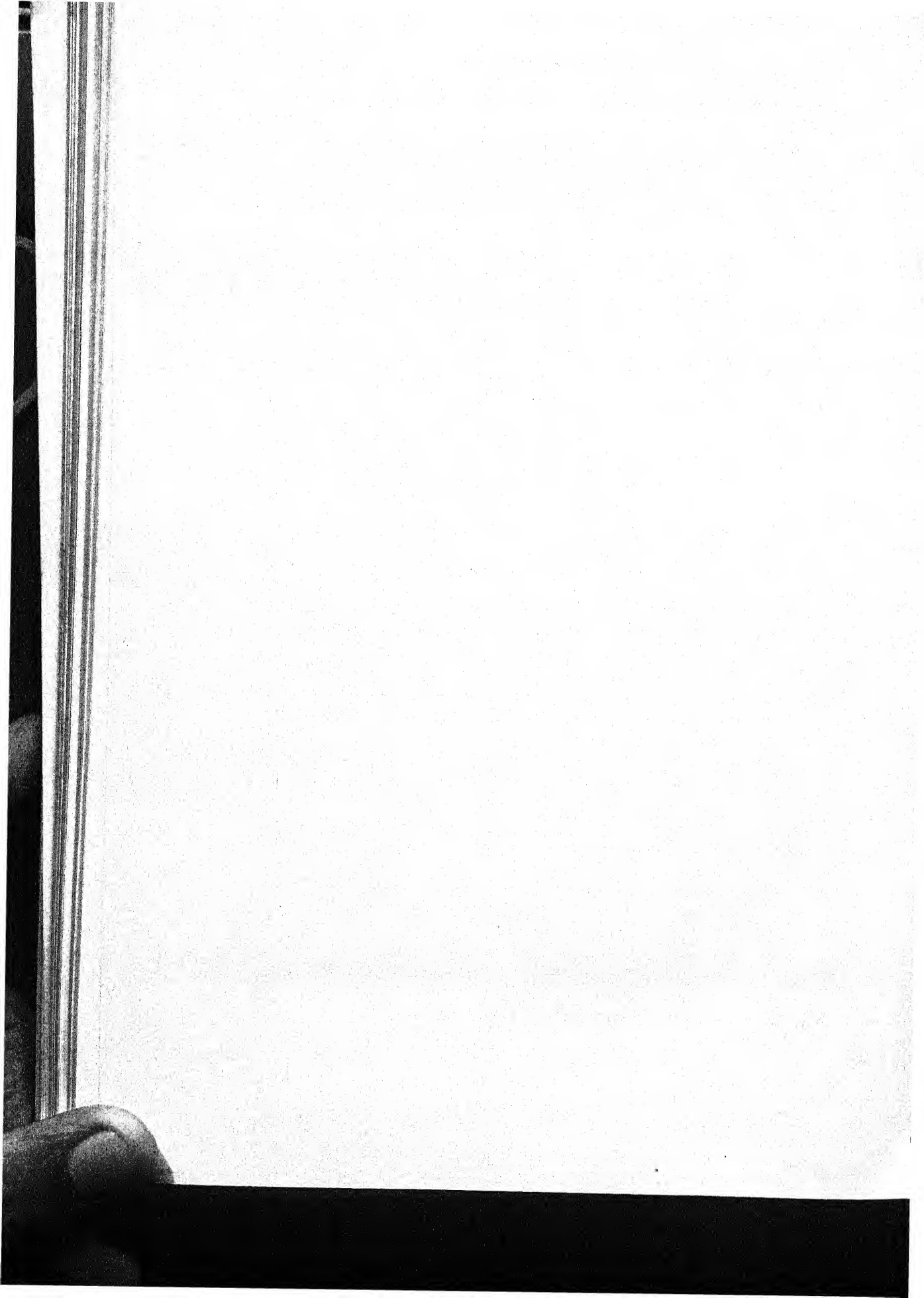
# MINERALOGY OF SOME SOILS FROM DENMARK, WESTERN AUSTRALIA

## DOROTHY CARROLL[1]

*Government Chemical Laboratories, Perth, Western Australia*

A soil survey covering about 27 square miles at Denmark, Western Australia (Lat. 34°57′ S., Long. 117°22′ E.), was made by Hosking and Burvill (6) as part of an investigation into the cause and control of a disease of stock, particularly dairy cows and sheep. This disease had been found to be confined to certain holdings. On one holding, stock would be severely affected, whereas on an adjacent property the animals would remain healthy. In fact, removal of affected stock to a sound holding resulted in rapid recovery.

The affected country lies in a hilly area which, in the virgin state, was heavily timbered with several species of *Eucalyptus*. Timber milling was the chief industry until 1904, by which time the best of the timber had been cut out. In 1909, the area was subdivided and thrown open for selection for agriculture with a view to pasture production and dairying. Early progress was slow, and in 1921 some dairy cattle were observed to be suffering from the obscure disorder (previously referred to), which was later to be known as the "Denmark wasting disease" or *enzootic marasmus*.

Notwithstanding the indications of the stock disorder, the generous rainfall (49 inches annually, with a favorable spread) and the apparent fertility of the soils made the district appear very attractive for closer settlement, particularly for dairying. Under the necessity of absorbing English migrants, it was included in the Western Australian Group Settlement Scheme in 1923. With the intensification of settlement, the stock disorder became more widespread and developed into such a serious problem that a comprehensive investigation was instituted by the State Department of Agriculture. Research by Filmer and Underwood (3, 4) showed that the Denmark wasting disease was the result of cobalt deficiency in the pasture. The soil survey of Hosking and Burvill established that, with a few anomalies, cobalt deficiency occurred on certain soil types, whereas others were generally sound.

The anomalies proved of such interest and importance that an explanation was sought in mineralogical examinations. The results of these examinations are reported in this paper.

## GEOLOGY AND TOPOGRAPHY

Denmark lies adjacent to the coast on the southern edge of the Pre-Cambrian

complex of Western Australia (fig. 1).   The following succession of rock forma-
tions occurs:

   (c) Dolerite, a sill cutting (a)
   (b) Sillimanite schist, quartzite⎫
                            ⎬ interbedded
   (a) Gneisses               ⎭

Gneisses are the principal outcropping rocks of the area and include several
varieties such as quartz-felspar gneisses, biotite gneisses, garnet gneisses, and a
basic gneiss or schist.   The dolerite is fresh and unmetamorphosed; it cuts the
gneisses (and possibly also the sillimanite schist and quartzite) as a sill about
300 feet thick, dipping fairly steeply to the northeast.   Remnants of this sill
occur on some of the hilltops.
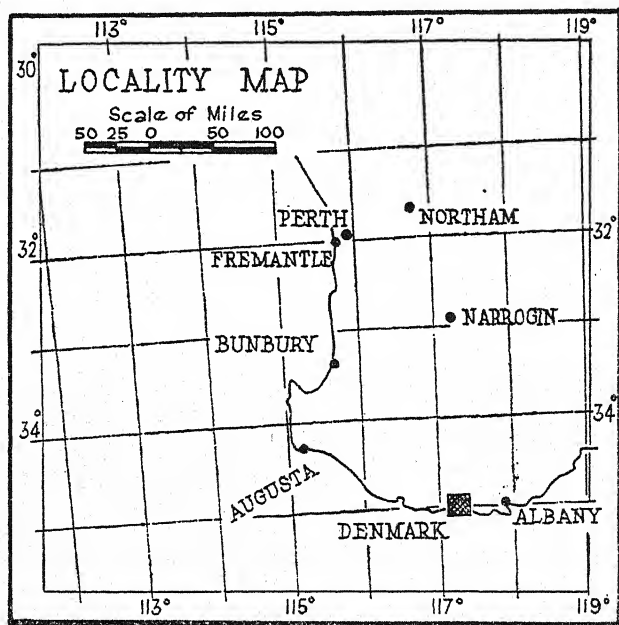


FIG. 1. LOCALITY MAP OF SOUTHWESTERN AUSTRALIA SHOWING THE
POSITION OF THE AREA DESCRIBED

   The area was at one time covered with a capping of laterite, but much of this
has been broken up and removed in the course of dissection.   The remains are
still an important feature.

   There is no geological map of the area, but observations have been made by
Blatchford (1) and by Hosking and Burvill (6).   It is noteworthy that the Pre-
Cambrian complex in this part of the state is deficient in metallic minerals such
as copper, lead, and zinc.

   Topographically the Denmark area is a ridge of hills, rising to 1,000 feet at
Mt. Shadforth, with associated valleys dissected by Scotsdale Brook and its
tributaries.   Most of the higher country is the slightly dissected surface of an
old peneplain which was once completely covered with laterite.   Where the

laterite has been removed by erosion, younger soils have developed on the newly exposed rocks. Even in these a certain amount of ironstone gravel is a common feature of the surface layers.

### SOILS

#### *Origin and texture*

Topographically there are three main groups of soils, as follows:

Soils developing *in situ* from the underlying rocks on hilltops and slopes.
Lateritic soils (soils consisting wholly or partly of the remains of the laterite capping previously mentioned) on the hilltops and adjacent slopes.
Wash, alluvial, and peaty swamp soils in the valleys.

Nine soils and a minor group which was not deemed sufficiently important or extensive to be named, were mapped by Hosking and Burvill (6) as indicated

TABLE 1

*Soil at Denmark, Western Australia*

| SOIL | CLASSIFICATION AS TO INCIDENCE OF COBALT DEFICIENCY | PARENT ROCK |
|---|---|---|
| Scotsdale | Sound | Dolerite and schists |
| Koorundurup | Sound | Dolerite and schists |
| Alluvial and wash | Sound | Various |
| Laterite boulder areas | Sound | Various |
| Wakundup | Unsound | Gneisses |
| Koorrabup | Unsound | Gneisses |
| Kordabup | Unsound | Gneisses |
| Kwilalup | Unsound | Gneisses, quartzite, and transported sand |
| Plantagenet sand | Unsound | Transported sands |
| Unnamed sand | Unsound | Sillimanite schist |

in table 1. The soils, the mineralogy of which is described here, have the following textural features:

*Wakundup.* Weakly podzolized soils consisting of sands and sandy loams, with gravel in the surface and subsoil.
*Scotsdale.* Gravelly loam to gravelly sand and sandy loam overlying medium to light or heavy clay.
*Koorundurup.* Very gravelly sand and gravelly loam overlying heavy clay.
*Koorrabup.* Sand to very gravelly sand overlying sandy, medium, or heavy clay.
*Alluvial.* Fine sandy loam to loam overlying heavy clay.
*Unnamed sandy loam.* Sandy loam above a light clay with schistose fragments.

#### *Cobalt and copper status*

As the wasting disease was found to be due to cobalt deficiency, the actual amount of cobalt was determined in a number of air-dried soils by Harvey (5, pp. 387, 388). His findings are shown in table 2. Although the cobalt status of

only a relatively small number of soils was determined, the figures show that the "soils of the Denmark district, and especially those soil types predominating in affected holdings, are generally low in cobalt in comparison with presumably healthy soils" (5, p. 391).

TABLE 2

*Cobalt status of soils from Denmark and other localities in SW. Australia*

After Harvey (5)

| LOCALITIES | CLASSIFICATION AS TO INCIDENCE OF COBALT DEFICIENCY | Co | NUMBER OF SAMPLES | SOIL |
|---|---|---|---|---|
| | | *p.p.m.* | | |
| | Sound | 12.1 | 6 | Alluvial and wash |
| | | 3.2 | 6 | Scotsdale |
| | | 32.0 | 1 | Koorundurup gravelly loam |
| | | 1.8 | 2 | Koorundurup gravelly sand |
| Denmark | Unsound | 0.6 | 5 | Wakundup gray gravelly sand |
| | | 0.8 | 4 | Wakundup brown gravelly sand |
| | | 0.5 | 1 | Unnamed sandy loam |
| | | 1.0 | 3 | Laterite boulder areas |
| | | 1.0 | 4 | Koorrabup |
| Pallingup and Gnowangerup | Sound | 8.4 | 15 | |
| Toodyay | Sound | 26–28 | | |
| Bridgetown | Sound | 40.0 | | |

TABLE 3

*Cobalt, nickel, copper, and manganese in Denmark soils*

After Hosking and Burville (6)

| SOIL | Co | Ni | Cu | Mn |
|---|---|---|---|---|
| | *p.p.m.* | *p.p.m.* | *p.p.m.* | *p.p.m.* |
| Wakundup......................... | 0.0 | 0.8 | 5.9 | 57 |
| Wakundup......................... | 0.0 | 2.4 | 5.0 | 176 |
| Wakundup......................... | 0.8 | 6.5 | 10.3 | 724 |
| Scotsdale......................... | 0.6 | 13.0 | 21.0 | 480 |
| Koorrabup......................... | 0.0 | 2.4 | 6.8 | 207 |
| Kordabup......................... | 0.0 | 0.6 | 6.6 | 21 |

A few copper figures are available for clover (*Trifolium subterraneum*) grown in the area, but these are not from any of the holdings from which soils were collected for mineralogical examination. The status varies from low normal to high normal (4.5 to 15.0 p.p.m. Cu), the figure for clover grown on a Wakundup soil being 5.3 p.p.m. Cu (8, p. 254). Figures given by Hosking and Burvill (6, p. 79) for Co, Ni, Cu, and Mn in the HCl extract of a few soils are shown in table 3.

## MATERIALS AND METHODS OF MINERALOGICAL EXAMINATION

### Collection of soils

Samples of soil and rocks were collected from areas of the various soils on both sound and unsound holdings (table 4).   The surface soils were taken to a depth of 6 to 9 inches and represented the $A_1$ and $A_2$ horizons.   A few samples were taken at a depth of several feet in two or three holdings where anomalous conditions had been reported.

### Laboratory procedure

The material approximating International fine sand (0.2 to 0.02 mm. diameter) was obtained by sieving and washing to remove the clay, some of the silt, and the organic matter.   This fine sand was then boiled in 1:1 concentrated HCl to remove the ferruginous coloring matter, dried, and a sample weighed out for bromoform separation, the heavy residue from which was also weighed to give the heavy fraction (see table 5).   The heavy fraction was tested for magnetite,

#### TABLE 4
*Soil samples collected in the Denmark district*

| SOIL | NUMBER OF SAMPLES | WHERE COLLECTED |
|---|---|---|
| Wakundup............ | 12 | Locs. 342, 436, 463, 461, 452, 386, 380, 693, 470, 468 |
| Scotsdale............ | 21 | Locs. 431, 524, 380, 465, 466, 424, 453, 455, 460, 693, 516, 370, 425 |
| Koorundurup.......... | 4 | Locs. 369, 428, 432 |
| Koorrabup........... | 4 | Locs. 557, 583, 510, 386 |
| Alluvial.............. | 1 | Loc. 386 |
| Unnamed sand......... | 1 | Loc. 575 |
| Kwilalup sand......... | 1 | Loc. 466 |

which was removed prior to mounting for microscopic identification of the grains. The approximate percentage composition of the nonmagnetic heavy fraction was obtained by counting the individual grains.

#### MINERALOGY OF THE FINE SANDS

The *heavy fractions* of the fine sands contained the following minerals: magnetite, ilmenite (plus limonite, leucoxene, etc.), zircon, amphibole, epidote and zoisite, augite, mica, garnet, tourmaline, sphene, rutile, kyanite, sillimanite, staurolite, spinel, corundum, andalusite, chlorite, and anatase.   The variation in mineral composition of the nonmagnetic residues is given in table 5.

It can be seen that both heavy and magnetic fractions are greatest in the soils derived from dolerite, and the figures are comparable to those given by Hosking and Burvill (6, table 15).   It is apparent from the mineral composition that some of the soils, for example, the Scotsdale, vary considerably, a point which will be discussed later.

The *light fractions* consist of varying proportions of quartz and felspar (micro-

TABLE 5

*Heavy minerals in the fine sands of Denmark soils*

COMPOSITION OF NONMAGNETIC HEAVY RESIDUE (columns Ilmenite through Amatase)

| Condition of holding for stock | Sample number | Location number | Heavy fraction % | Magnetic fraction % | Ilmenite, etc. % | Zircon % | Amphibole % | Epidote, Zoisite % | Augite % | Mica % | Garnet % | Tourmaline % | Sphene % | Rutile % | Kyanite % | Sillimanite % | Staurolite % | Spinel % | Corundum % | Andalusite % | Chlorite % | Amatase % | Soil as mapped |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Group 1, sound | 19 | 431 | 40 | 30 | 87 | 2 | 0.4 | | 8.5 | | 0.8 | | | 0.4 | | | | | | | | | Scotsdale |
| | 38 | 516 | 40 | 35 | 67 | 4 | | | | 28 | | 0.5 | | 0.2 | | 0.2 | | | | | +* | | Scotsdale |
| | 39 | 524 | 21 | 2.6 | 78 | 17 | | | | 2 | 0.2 | 0.2 | 0.4 | 0.4 | | 0.4 | | | | | | | Scotsdale |
| | 42 | 369 | 25.4 | 22 | 91 | 6 | + | | | 0.2 | 0.2 | 0.4 | | | + | 0.2 | 0.2 | | | | | | Koorundurup |
| | 45 | 386 | 0.7 | 0.2 | 57 | 37 | 0.2 | 0.5 | | | + | 1.5 | 2 | 0.9 | 0.2 | 0.3 | + | | | | | | Koorrabup |
| | 46 | 386 | 5.2 | 3.5 | 82 | 12 | + | 2 | | | | 0.3 | 0.8 | 0.5 | 1 | | 0.3 | + | | | | | Alluvial |
| | 47 | 386 | 0.7 | 0.2 | 60 | 33 | 0.5 | 0.9 | | | | 0.2 | 0.9 | 1.7 | | 0.5 | 0.1 | + | | 0.1 | | | Wakundup† |
| | 51 | 380 | 3.4 | 2.5 | 65 | 25 | 1 | 3 | | | + | 0.5 | 1 | 2.4 | 0.2 | | | | | | | | Wakundup† |
| | 54 | 380 | 42 | 39 | 94 | 3 | 0.4 | 0.2 | 0.4 | | | 0.7 | | 0.9 | | 0.2 | | | | | 0.2 | | Scotsdale |
| | 57 | 428 | 28 | 18 | 60 | 2 | 8 | | 0.2 | 29 | | | 0.2 | | | | | | | | | | Koorundurup |
| | 60 | 428 | 37 | 25 | 60 | 8 | 21 | 1 | 5 | + | | | | 1.6 | | | | | | 1.6 | | | Koorundurup |
| | 62 | 432 | 25 | 22 | 76 | 20 | 0.6 | 0.1 | + | | + | 0.3 | | 2 | + | | | 0.1 | | | 0.1 | | Koorundurup |
| | 63 | 465 | 1.2 | + | 62 | 28 | 0.8 | 0.5 | 7 | | + | | | 0.5 | 0.5 | | | | | | 0.5 | | Scotsdale |
| Group 2, unsound | 16 | 342 | 0.4 | 0.1 | 43 | 46 | 0.5 | 2.6 | | | | 0.2 | 1 | 0.5 | 4 | 0.2 | | 1 | 0.2 | | | | Wakundup |
| | 21 | 436 | 5 | 2.5 | 13 | 77 | 0.2 | 0.7 | | 0.4‡ | 6§ | 0.6 | 0.7 | + | | | + | | | | | | Wakundup |
| | 25 | 463 | 1 | 0.6 | 21 | 75 | 0.4 | 0.3 | | | 0.3 | 1 | 0.9 | 0.6 | 0.1 | 0.1 | + | | | | | | Wakundup |
| | 27 | 461 | 13.4 | 4.5 | 7 | 3 | | | 88 | | | + | + | 0.2 | | | | | | | | | Wakundup |
| | 29 | 461 | 0.4 | 0.2 | 19 | 59 | + | | 12 | | | + | 2 | 5.6 | 0.9 | | | + | | | | | Wakundup |
| | 31 | 452 | 0.3 | 0.1 | 13 | 72 | + | | 4 | | 2 | 0.8 | 1.5 | 1 | 0.2 | 0.2 | 0.6 | | | | | 0.2 | Wakundup |
| | 32 | 453 | 0.8 | 0.2 | 14 | 83 | 0.2 | | | | 1 | 0.2 | 0.2 | 0.9 | | | | | | | | 0.3 | Scotsdale |
| | 34 | 575 | 2.2 | 0.2 | 20 | 6 | | 0.5 | | | 0.5 | 1 | 2 | 0.3 | | | 67 | | | | | 0.3 | Unnamed sand |
| | 35 | 557 | 0.9 | + | 17 | 68 | | | | | 0.2 | 1 | 1.5 | 3 | 7 | 0.2 | 0.2 | | | | | | Koorrabup |
| | 40 | 583 | 0.7 | 0.2 | 18 | 77 | 0.2 | 0.2 | | | 0.5 | 0.5 | 1 | + | 0.2 | 0.4 | | + | + | | | | Koorrabup |
| | 41 | 510 | 1.5 | 0.7 | 26 | 66 | 0.6 | 0.8 | | | 1.5 | 0.6 | 0.8 | 2 | 0.1 | 0.3 | | + | + | 0.1 | | 0.1 | Koorrabup |
| | 43 | 370 | 2.6 | 1.7 | 29 | 60 | 7 | 2 | | | + | 0.6 | 1 | 0.2 | + | 0.2 | | + | + | | | | Scotsdale |
| | 66 | 465 | 1.0 | 0.1 | 11 | 83 | 0.1 | 0.5 | | + | 0.5 | 0.5 | 3 | 0.5 | + | 0.1 | | | | 0.2 | | | Scotsdale |
| | 68 | 466 | 1.4 | 0.4 | 8 | 84 | | 0.3 | | | 0.1 | + | 6 | 0.8 | | 0.3 | | | | | | | Scotsdale |
| | 69 | 466 | 1.6 | 0.8 | 10 | 80 | 0.9 | 0.2 | | + | 0.9 | 1 | 5 | 0.7 | 0.3 | 0.1 | | | | | | | Scotsdale |
| | 73 | 693 | 1.0 | 0.5 | 17 | 74 | 2 | 0.3 | | 0.3 | 1 | 1 | 1.5 | 1.5 | + | | | 0.1 | 0.1 | | | | Wakundup |
| | 81 | 466 | 0.4 | + | 13 | 82 | | | | | | 0.3 | 2 | 0.3 | | 0.6 | 0.3 | | | | | | Kwilalup sand |
| Group 3, from appearance thought to be sound‖ | 74 | 693 | 0.6 | 0.4 | 43 | 44 | 3 | 0.5 | | + | 0.3 | 1.7 | 2 | 2 | | 0.1 | 0.1 | | | | | | Scotsdale |
| | 75 | 693 | 0.8 | 0.5 | 27 | 62 | 0.7 | 0.3 | 0.1 | 0.1 | 0.1 | 2.5 | 3 | 3 | + | 0.1 | 0.3 | + | | | | | Scotsdale |
| | 76 | 693 | 1.2 | 0.8 | 40 | 50 | 0.6 | 0.1 | | 0.1 | + | 1 | 2 | 4 | 0.1 | 0.5 | | | 0.1 | | 0.1 | | Scotsdale |
| | 80 | 424 | 0.5 | 0.2 | 58 | 27 | 2 | | 3 | | | 3.7 | 1 | 3 | | 0.4 | | | | | 0.1 | | Scotsdale |
| | 82 | 453 | 0.7 | 0.2 | 14 | 82 | 0.2 | | | | | 0.8 | 0.5 | 0.3 | 1 | | 0.3 | | | | | | Scotsdale |
| | 84 | 455 | 0.8 | 0.3 | 9 | 86 | 0.6 | 0.2 | | | 1.6 | 1 | | 0.2 | 0.6 | | | | | | | | Scotsdale |
| | 85 | 455 | 0.6 | 0.3 | 14 | 81 | 0.4 | 1 | | | | 0.6 | 1.3 | 0.4 | 0.2 | | 0.2 | | | | | | Scotsdale |
| | 86 | 693 | 1.9 | 0.9 | 18 | 42 | 34 | 4 | | | 0.2 | 0.8 | | 0.4 | | | | | | | | | Scotsdale |
| | 88 | 693 | 0.7 | 0.6 | 32 | 60 | 0.4 | 0.4 | | | 0.4 | 2 | 0.8 | 1.5 | | 0.2 | 0.2 | | | | | | Scotsdale |
| | 93 | 693 | 0.5 | 0.3 | 50 | 41 | 0.4 | 2 | | | 0.7 | 2 | 1 | 0.7 | | 0.7 | | | | | | | Scotsdale |
| | 95 | 693 | 1.2 | 0.9 | 61 | 34 | 0.2 | | | | 0.7 | 0.5 | 1.6 | 0.2 | | 0.2 | | | | 0.2 | | | Scotsdale |
| Group 4, from appearance thought to be unsound¶ | 97 | 470 | 0.8 | 0.2 | 12 | 84 | 0.4 | 0.2 | | | 0.9 | 0.2 | 0.4 | 0.5 | 0.2 | 0.2 | | | | | | | Wakundup |
| | 99 | 470 | 2.0 | 1.3 | 7 | 81 | 2 | 0.4 | | | 7§ | | 0.2 | 0.4 | 0.2 | 0.2 | | | | | | | Wakundup |
| | 103 | 470 or 468 | 2.5 | 1.6 | 16 | 75 | 0.2 | | | | 0.4 | 0.6 | 5 | 2 | | 0.4 | | 0.2 | 0.2 | | | | Wakundup |

\* + indicates presence of the mineral, but in very small amounts.
† The holding contains other soils in addition to the Wakundup.
‡ Most of the mica goes into the light fraction.
§ About one third of the magnetic fraction also consists of garnet.
‖ Soil type identified in field considered sound, but holding proved unsound.
¶ Soil type identified in field considered unsound, but holding proved to be sound.

*Note:* The figures given for the composition of the nonmagnetic heavy residue do not total 100 per cent because of omission of grains not completely identified and simplification of other figures.

cline, orthoclase, microperthite, and acid plagioclase). The soils derived from gneisses generally contain a variable proportion of rounded quartz grains, some almost spherical, which suggest their original sedimentary nature. In the soils derived from dolerites there is much altered mineral matter, possibly a chlorite or a mixture of chlorite and a clay mineral (? nontronite) which is considered to be altered augite in part. Most of the clay minerals have been removed during cleaning and preparation of the samples.

### Notes on individual minerals

*Magnetite.* The magnetic fraction is given in table 5 as a percentage of the fine sand in which it is almost invariably present in amounts from a trace to 39 per cent. In one soil at least (no. 21), garnet was removed with the magnetite by the small electromagnet used. In some soils magnetite is the most plentiful heavy mineral, its presence resulting from the decomposition of dolerite, and it therefore serves to distinguish soils of this origin from others in the area.

*Ilmenite,* including other opaque minerals such as limonite, leucoxene, and unidentified grains, makes up a large part of some of the nonmagnetic residues (see table 5), but this is a usual occurrence for soils of Western Australia. There is a considerable variation in the proportion of opaque to nonopaque grains in the heavy fractions, and this can be used to differentiate members of the same soil series having a somewhat different parentage. Several groups of soils could be distinguished according to the percentages of opaque and nonopaque minerals. These groups are given in table 6.

*Zircon* is the most characteristic mineral of the majority of the soils from this area, particularly those of the Wakundup series, in which it usually ranges from 33 to 84 per cent of the heavy nonmagnetic residues and averages 60 per cent. The varietal features are interesting, and several distinct types were noted, which assisted in differentiating the soils mineralogically. The most conspicuous of these types is the purplish brown pleochroic zircon, which in some residues is as high as 75 per cent of the total zircon present; generally, however, the proportion is much lower. Similar types of zircon occur in the gneisses of the area. Koorrabup soils contain zircon rather similar in appearance to the types in the Wakundup soils.

In the soils mapped as Scotsdale there are two distinct mineral assemblages. One, obviously derived from dolerite, contains very few zircons, and these are sharply angular and flattish in appearance because of enlarged prism faces and reduced pyramid faces. The other is not of doleritic origin but probably formed from a basic schist and has zircons similar in appearance to those of the Wakundup soils, but in one (no. 32 from loc. 453) there is a very large proportion of strongly colored zircons in both the surface and the subsoil. The mineralogical examination shows that the Scotsdale should be divided into at least two soil series.

The Koorundurup soils are similar mineralogically to the Scotsdale soils formed on dolerite.

The alluvial soils contain several different types of zircon, zoned, sharply prismatic and unworn, and a few rounded grains. The sillimanite schist contains a distinct type of zircon, colorless, rounded, and nearly equidimensional.

Zircon affords a useful means of distinguishing between the soils derived from the gneissic series and those derived from dolerite. Scotsdale varieties (a) and (b) are evidently derived from schists associated with the gneisses, and seem to be more closely related mineralogically to the Wakundup than to the Scotsdale soil derived from dolerite.

*Amphibole* (hornblende), varying from pale green to brownish green, and sometimes partly or completely chloritized, occurs in small quantities in many of the soils, but is abundant only in soils closely associated with hornblende schists or other hornblende-bearing rocks. The largest quantities are in samples 27, 43, 57, 60, and 86. Sample 27 represents a soil derived from a hornblende schist

TABLE 6

*Amount of opaque and nonopaque heavy minerals in the fine sand residues of Denmark soils*

| SOIL | NUMBER OF SAMPLES | OPAQUE | NONOPAQUE | HEAVY FRACTION | MAGNETIC FRACTION |
|---|---|---|---|---|---|
| | | *per cent* | *per cent* | *per cent* | *per cent* |
| Wakundup (high % opaques) | 3 | 56 | 44 | 1.5* | 0.9 |
| Wakundup (low % opaques) | 9 | 14 | 86 | 2.9† | 1.3 |
| Scotsdale (dolerite) | 4 | 81 | 19 | 36.0 | 27 |
| Scotsdale (variety a) | 7 | 49 | 51 | 0.8 | 0.4 |
| Scotsdale (variety b) | 10 | 14 | 86 | 1.2 | 0.5 |
| Koorundurup | 4 | 72 | 28 | 29.0 | 22 |
| Koorrabup | 4 | 29 | 71 | 0.9 | 0.3 |

* The figures for this average are 0.4, 0.7, and 3.4 and the given average is therefore rather too high.

† The figures included 13.4 per cent for one sample, which makes the heavy fraction rather higher than it should be.

interbedded with gneiss in an area of Wakundup soil; no. 43 is from a Scotsdale soil; nos. 57 and 60 are from a Koorundurup soil; and no. 36 is from near an outcrop of hornblende schist in an area of Scotsdale soil.

*Epidote and zoisite* occur in small quantities in most of the soils, the amount rising to 12 per cent in a Wakundup soil from location 461. These minerals have the usual features and generally are either irregular or prismatic in form. Zoisite is less plentiful than epidote, but some composite grains include both varieties.

*Augite.* Soils of the Scotsdale and Koorundurup series that are derived from dolerite contain augite. In two of these soils (nos. 38 and 57), the amounts are conspicuous. Augite generally weathers rather readily and is absent from mature soils, even if originally present in the parent rock. In the soil the augite is grayish brown and altered at the edges. It is present in two rocks collected from

the area, a hornblende-pyroxene gneiss (basic gneiss) and, more plentifully, in the dolerite.

*Mica* (biotite) occurs in a number of soils derived from gneisses but, because of its flaky nature, is likely to be lost during preparation of the residue. It is a prominent constituent in some of the gneisses, but apparently weathers rather readily and is generally not very conspicuous in the residues.

*Garnet* in fresh, angular fragments, colorless or pale pink, and with few inclusions, is found in small amounts in most of the soils derived from gneisses; and in two soils directly associated with garnetiferous gneisses (nos. 21 and 99) it comprises 6 and 7 per cent respectively of the heavy fraction, in addition to being present in the magnetic fraction. In the remaining soils, the percentage is fairly uniform.

*Tourmaline.* The heavy fractions of most of the soils contain a small and fairly uniform amount of tourmaline in gray or brown grains. The most conspicuous amount is in a Scotsdale soil, variety (a), which contains over $3\frac{1}{2}$ per cent.

*Sphene* is fairly plentiful, particularly in those soils that are derived from gneisses. It occurs in chunky colorless grains.

*Rutile* occurs in small but fairly uniform quantities in most of the heavy fractions, rising to 4 per cent in a Wakundup and in a Scotsdale soil. Generally it has rather a worn appearance and varies from reddish to yellowish brown in color. In some residues there are fresh prismatic grains or irregular masses without crystal faces.

*Kyanite* in colorless grains occurs in amounts up to $\frac{1}{2}$ per cent in a number of the residues of the Wakundup, Koorrabup, and varieties of Scotsdale soils. The grains are typical and some are worn.

*Sillimanite* occurs in typical grains and in small quantities in a number of the soils, but in one residue (no. 34) it makes up to 67 per cent and serves to differentiate this soil (the unnamed sand) from all others in the area. Sillimanite-schist outcrops nearby and is also found in other places. The sillimanite in the residue was not associated with kyanite.

*Staurolite* is a minor constituent of these residues and usually accompanies kyanite, to which it is about equal in amount. It varies from pale to deep brown and is angular.

*Spinel* is present in a few of the soil residues as odd grains pale to deeper green and generally of a somewhat worn appearance.

*Corundum.* Small pale blue grains of corundum occur in several of the residues, generally accompanying spinel.

*Andalusite*, in typical slightly pleochroic grains, occurs in two of the residues only.

*Chlorite* was identified in small amounts in a number of the Scotsdale and Koorundurup soils. As noted under amphibole, chlorite often accompanies this mineral, and composite grains may occur.

*Anatase* is present in a few of the residues, the greatest amount being in the residue from the unnamed sand.

### SIGNIFICANCE OF THE HEAVY MINERALS IN THE FINE SANDS

In the soils examined there are two well-defined assemblages of heavy minerals. One of these is characteristic of soils derived from gneisses and schists; the other, of soils derived from dolerite.

| *Soils derived from gneisses and schists* | *Soils derived from dolerite* |
| --- | --- |
| Magnetite | Magnetite |
| Ilmenite | Ilmenite |
| Zircon | Augite |
| Amphibole | Rutile |
| Epidote | Amphibole |
| Zoisite | |
| Mica | |
| Garnet | |
| Tourmaline | |
| Sphene | |
| Rutile | |
| Kyanite | |
| Sillimanite | |
| Staurolite | |
| Andalusite | |
| Spinel | |
| Corundum | |

The varietal features of the minerals have been described in the preceding pages. A consideration of these, together with the percentage composition of the nonmagnetic heavy residues, gives a clear picture of soil parentage, and mineralogical types can be distinguished even though the soil profiles appear similar. This method of differentiating soils is possible because in this area most of the soils are sedentary. As an example, compare nos. 27 and 29, and nos. 51 and 54 in table 5. The soils of each pair were collected within a few hundred yards of each other.

The soil survey of Hosking and Burvill (6) showed that it is on the soils derived from gneisses in the Denmark area that the wasting disease develops. The soils involved are the Wakundup, Koorrabup, Kordabup, and Kwilalup. The Scotsdale, Koorundurup, and alluvial soils are generally sound. In a number of holdings the soil profiles exhibited the general features of the Scotsdale and were mapped as such. The mineralogy indicated, however, that the parent material was not dolerite, but a deeply weathered schist.

### *The Scotsdale soils*

The Scotsdale soils occur in one large area and a number of smaller areas. The soils all have similar profile features, but mineralogically comprise three varieties (tables 6 and 7).

The main Scotsdale soil is derived from dolerite, but, as mentioned previously, the parent rock of mineralogical varieties (a) and (b) is not known. The depth of weathering and the micaceous appearance of the B-C horizon suggest that these soils are derived from chloritic or talcose schists belonging to and interbedded with the gneisses, sillimanite schist, and quartzite.

Very few cobalt analyses are available for the Scotsdale soils.   Soil from the same holding as no. 39 contained 5 p.p.m. Co, but this soil differs somewhat from the other true Scotsdale soils examined mineralogically, and therefore it cannot be considered representative.   Soil from the same holding as no. 32 [Scotsdale variety (b)] contains 2 p.p.m. Co, a figure several times greater than that obtained for any Wakundup soil, although actually there are few outstanding mineralogical differences.

One holding apparently on Scotsdale soil, and therefore expected to be sound, reported severe wasting disease.   A mineralogical examination showed (see nos.

TABLE 7

*Variation in heavy mineral content of the Scotsdale soils*

| SOIL | SAMPLE NUMBER | INDEX FIGURE* | REMARKS |
|---|---|---|---|
| | | *per cent* | |
| Scotsdale dolerite | 19 | 40 | Opaque minerals and augite prominent in the nonmagnetic residue |
| | 38 | 40 | |
| | 39 | 21 | |
| | 54 | 42 | |
| Scotsdale variety (a) | 63 | 1.2 | Opaque to nonopaque minerals in the nonmagnetic residue is approximately 50:50; zircon prominent |
| | 74 | 0.6 | |
| | 75 | 0.8 | |
| | 76 | 1.2 | |
| | 80 | 0.5 | |
| | 93 | 0.5 | |
| | 95 | 1.2 | |
| Scotsdale variety (b) | 32 | 0.8 | The nonmagnetic residue contains a relatively low percentage of opaque minerals; zircon very prominent |
| | 43 | 2.6 | |
| | 66 | 1.0 | |
| | 68 | 1.4 | |
| | 69 | 1.6 | |
| | 82 | 0.7 | |
| | 84 | 0.8 | |
| | 85 | 0.6 | |
| | 86 | 1.9 | |
| | 88 | 0.7 | |

* Per cent by weight of heavy residue in the fine sand.

73–76, 88, 93, 95 in tables 5 and 7) that the soil has not been derived from dolerite, but partly from gneiss and partly from a deeply weathered schist.   There is an indication that some material from a Wakundup soil higher up the slopes has spread over a profile of the Scotsdale (7, p. 44).

*The Wakundup soils*

The Wakundup soils, which cover more than one quarter of the area surveyed, can be divided mineralogically into two varieties: (a) with a large percentage of opaque minerals; and (b) with a small percentage of opaque minerals (see

table 8).  Detailed mapping of the bands of gneiss would assist in defining these two varieties of Wakundup.

The Wakundup soils are generally considered unsound, and, as has been mentioned, are derived from members of the gneissic formation.  In one holding, however, the Wakundup soils proved to be sound.  Here, though the principal rock outcropping is gneiss, remnants of dolerite with much dark ferruginous gravel occur.  These remnants, on weathering, have released sufficient nutritive elements to give sound pastures.  Hosking and Burvill found (6, p. 79) that a soil from this area was richer in cobalt than the normal Wakundup soils.  The mineralogical examination showed that these soils (nos. 99, 103, tables 5 and 8), although largely derived from garnet gneiss, contain unusually large amounts of heavy fraction and magnetite (7, p. 43).

TABLE 8

*Variation in heavy mineral content of the Wakundup soils*

| SOIL | SAMPLE NUMBER | INDEX FIGURE* | REMARKS |
|------|---------------|---------------|---------|
|      |               | *per cent*    |         |
| Wakundup | 16 | 0.4 | Zircon is prominent in all these residues, |
| variety (a) | 47 | 0.7 | both (a) and (b) |
|      | 51 | 3.4 |         |
| Wakundup | 21 | 5.0 | High figure is due to garnet |
| variety (b) | 25 | 1.0 |         |
|      | 27 | 13.4 | High figure is due to hornblende |
|      | 29 | 0.4 |         |
|      | 31 | 0.3 |         |
|      | 73 | 1.0 |         |
|      | 97 | 0.8 |         |
|      | 99 | 2.0 | High figures are due to contamination from |
|      | 103 | 2.5 | dolerite |

* Per cent by weight of heavy residue in the fine sand.

### DISCUSSION OF COBALT DEFICIENCY IN DENMARK SOILS

The Pre-Cambrian complex in the extreme southwest of Western Australia has, with the exception of minor quantities of lead and zinc in one area and some tin and tantalum in another, no metalliferous country.  The tin and tantalum are associated with the intrusion of younger granite and pegmatite into the ancient gneisses, which are largely of sedimentary parentage.  The nearest copper, cobalt, manganese, and gold ores occur about 180 miles northeast of the Denmark area.

Probable reasons for the cobalt deficiency of the soils derived from gneisses in the Denmark area can be suggested by a consideration of the distribution of trace elements in rocks of the earth's crust.  Minute quantities of such metals as copper, lead, zinc, and cobalt occur in many rocks, where they enter into the lattice structure of the ferromagnesian minerals (amphibole, pyroxene, olivine) according to well-defined rules.  A summary of the geochemical approach to problems of animal ecology was made in 1940 by Thomas (9) and was further

amplified by Carroll (2). The geological or geochemical aspect of deficiency problems appears to be particularly important in southwestern Australia, a peneplaned region with extensive areas of sedentary soil. The mineral matter in a sedentary soil depends on the composition of the parent rock; if the parent rock can supply a variety of trace or minor elements, then the availability depends on the weathering processes in soil formation and the mobilization of these elements in the surface soil by the action of successive generations of the vegetative layer. If the parent rock is deficient in one or several minor elements necessary to animal and/or plant growth, then the soil resulting from such a rock must also be deficient where its sedentary nature can be demonstrated.

Another factor of great importance is the susceptibility to weathering of the parent rock, which depends on the type of rock and on the climatic and topographic conditions under which the weathering takes place. At Denmark there have been two distinct periods of soil formation: first, laterite formed some time during the Tertiary; and secondly, soils formed in recent times on parent rocks from which the laterite capping has been removed. Gravelly soils represent the intermediate stage in the disappearance of laterite and the formation of modern soils. Sandy transported soils in the lower parts of the area are of mixed origin and probably include material from the old A horizon of the laterite formation together with later weathering products.

The chemical composition of the parent rocks appears to be of fundamental importance in the Denmark soils. The sound or healthy soils which are sedentary (Scotsdale and Koorundurup) are derived from a fresh unmetamorphosed intrusion of dolerite, which contains abundant augite and felspar weathering readily to supply the necessary chemical elements. The few cobalt figures obtained for these soils are relatively high. The unsound or unhealthy soils (Wakundup, Koorrabup, etc.) are derived from gneisses which are, in part at least, metamorphosed sediments derived from unknown sources in rocks prior to metamorphism. There are, it is true, bands in these gneisses which appear to represent igneous intrusions in the sedimentary series, but large areas consist only of acid gneisses, the ferromagnesian content of the majority of which is not high. Most of the ferromagnesians have arisen by recrystallization during metamorphism. It can be assumed with reasonable certainty that the ferromagnesians in the gneisses differ markedly in chemical composition and particularly in minor element content from ferromagnesians crystallized from a magma. When a mineral crystallizes in any environment it can take into its structure very minute quantities of other elements, *e.g.*, traces of Cu in augite, or Ni in olivine. A magma of intermediate or basic composition is much more capable of supplying minute quantities of such elements as Cu, Co, Ni, and Zn than are sediments and granitic materials, although it is probable that some new material may be added during metamorphism, if the resulting rocks include migmatites.

## CONCLUSIONS

The mineralogy of the fine sands of the principal soils of the Denmark area, Western Australia, indicates that a geological approach is important in the interpretation of the incidence of wasting disease (enzootic marasmus) due to Co

deficiency in areas of sedentary soil on a peneplain surface. Variation in composition of the parent rock is reflected in the mineral content of such soils, even though the soil profiles may have a similar appearance. In one soil (the Scotsdale) three mineralogical types were distinguished. Anomalous incidence of wasting disease on certain holdings can be explained as a result of mineralogical examinations. Theoretical reasons for the Co deficiency in the area are given.

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# SUPPLEMENTS TO HIGH-ANALYSIS FERTILIZERS WITH SPECIAL REFERENCE TO SULFUR, CALCIUM, MAGNESIUM, AND LIMESTONE[1]

N. J. VOLK, J. W. TIDMORE AND D. T. MEADOWS[2]

*Alabama Agricultural Experiment Station*

With the increased use of high-analysis fertilizers such as triple superphosphate, 60 per cent muriate of potash, ammonia liquors, urea, and ammonium nitrate, the need for the application of supplementary plant-food elements to the soil will undoubtedly become increasingly important and may become a major factor in plant production on certain soil types. Cooperative tests with cotton conducted by Williamson, Bertram, and Richardson[3] definitely showed that sulfur became deficient in many soils in Alabama when triple superphosphate, sodium nitrate, and muriate of potash were used as sources of P, N, and K, respectively. Other unpublished data indicate that calcium and magnesium are deficient in certain soil types in Alabama. It is also an established fact that the acidity of fertilizers should be corrected with lime or other neutralizing agents when acid-forming fertilizers are used on noncalcareous soils. There are indications that minor-element deficiencies are becoming more and more pronounced over greater areas of agricultural land, and it appears logical to conclude that the use of high-analysis fertilizers will aggravate this situation.

A large amount of work has been done in different parts of the world on the problem of sulfur nutrition of plants and animals. As early as 1911, Hart and Peterson (2) drew attention to the possibility that sulfur deficiencies probably existed in certain regions of the United States. A general summary of the literature on sulfur is given by Alway (1), and an account of the sulfur industry, by Haynes (3).

This paper is a report of investigations conducted at the Alabama Agricultural Experiment Station for the purpose of determining the need for supplements to high-analysis fertilizers with special reference to sulfur, calcium, magnesium, and limestone.

## Amounts of sulfur brought down in rain

Especially designed gauges for collecting rain water for sulfur measurements were placed at 12 locations in Alabama (table 1); at Experiment, Georgia; at State College, Mississippi; and at Jackson, Tennessee. These gauges were

operated 4 years. The water was sent to Auburn monthly in glass containers, and its sulfur content was determined by oxidizing the sulfur and precipitating it as $BaSO_4$.

As Alabama is largely an agricultural state, only small amounts of sulfur were brought down in the rain in the rural districts. Over the 4-year period from 1940 to 1943, the amounts of sulfur brought down annually in rural districts ranged

TABLE 1

*Amounts of sulfur brought down in rain over the 4-year period, 1940 to 1943, inclusive*

| LOCATION | POUNDS OF $SO_3$ PER ACRE (AVERAGE FOR 4 YEARS) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Jan. | Feb. | Mar. | Apr. | May | June | July | Aug. | Sept. | Oct. | Nov. | Dec. | Total |
| Auburn, Alabama......... | 1.32 | 1.60 | 2.12 | 0.90 | 0.81 | 0.85 | 0.95 | 0.82 | 0.56 | 0.83 | 0.94 | 1.79 | 13.49 |
| Tennessee Valley Substation, Belle Mina, Alabama.............. | 1.08 | 1.09 | 1.73 | 1.57 | 1.36 | 1.43 | 1.49 | 1.02 | 0.70 | 0.85 | 1.07 | 2.19 | 15.58 |
| Birmingham, Alabama..... | 5.57 | 7.43 | 5.67 | 3.11 | 4.98 | 4.69 | 6.88 | 5.27 | 3.17 | 4.83 | 7.67 | 17.52 | 76.79 |
| Sand Mountain Substation, Crossville, Alabama..... | 1.36 | 1.42 | 2.21 | 1.28 | 1.06 | 1.26 | 1.06 | 1.24 | 0.34 | 1.11 | 0.94 | 1.80 | 15.08 |
| Gulf Coast Substation, Fairhope, Alabama...... | 1.01 | 1.13 | 1.69 | 1.34 | 0.97 | 1.38 | 1.36 | 0.78 | 0.98 | 1.58 | 0.66 | 1.77 | 14.65 |
| Wiregrass Substation, Headland, Alabama..... | 0.79 | 1.20 | 1.39 | 0.77 | 1.15 | 0.97 | 0.72 | 0.94 | 0.13 | 0.17 | 0.75 | 1.28 | 10.26 |
| Black Belt Substation, Marian Jct., Alabama... | 1.04 | 2.37 | 2.25 | 0.90 | 0.65 | 0.75 | 1.42 | 0.86 | 0.52 | 0.32 | 1.17 | 1.73 | 13.98 |
| Experiment field, Alexandria, Alabama.......... | 1.11 | 1.34 | 1.66 | 1.16 | 1.16 | 1.49 | 1.84 | 0.87 | 0.31 | 0.77 | 0.84 | 1.52 | 14.07 |
| Experiment field, Aliceville, Alabama.......... | 1.33 | 1.23 | 1.74 | 0.82 | 1.09 | 1.49 | 0.80 | 0.81 | 0.31 | 0.74 | 0.79 | 1.30 | 12.45 |
| Kinston, Alabama......... | 0.72 | 0.66 | 1.08 | 0.37 | 0.65 | 0.53 | 0.66 | 0.43 | 0.32 | 0.74 | 0.52 | 0.55 | 7.23 |
| Experiment field, Monroeville, Alabama......... | 0.98 | 0.79 | 1.89 | 0.81 | 1.07 | 1.24 | 0.50 | 0.90 | 0.68 | 0.34 | 0.46 | 1.15 | 10.81 |
| Experiment field, Prattville, Alabama.......... | 1.06 | 1.04 | 2.10 | 1.54 | 0.78 | 1.06 | 1.09 | 0.66 | 0.34 | 0.66 | 0.84 | 1.47 | 12.64 |
| Experiment, Georgia...... | 1.71 | 2.03 | 2.68 | 1.27 | 1.19 | 1.03 | 1.43 | 1.46 | 0.54 | 1.45 | 1.12 | 1.61 | 17.52 |
| State College, Mississippi.. | 0.79 | 1.53 | 1.49 | 1.07 | 0.98 | 0.84 | 2.16 | 0.76 | 0.55 | 0.59 | 0.95 | 1.16 | 12.87 |
| Jackson, Tennessee....... | 2.37 | 3.40 | 5.09 | 3.20 | 2.90 | 2.48 | 2.98 | 2.13 | 1.27 | 2.00 | 2.49 | 2.71 | 33.02 |

The authors express their appreciation for the assistance given by B. Hazelwood of Tennessee, Otto Sell of Georgia, and W. B. Andrews of Mississippi in obtaining the samples of rain water from their respective states.

from 7.23 pounds per acre at Kinston, Alabama, to 15.58 pounds per acre at Belle Mina, Alabama. These amounts are insufficient to replace the sulfur used by crops and leached away annually.

Data obtained from the analysis of water collected in the rain gauge in the city of Birmingham showed that 76.79 pounds of sulfur were brought down annually. That amount, of course, would be sufficient for crop needs in that immediate vicinity.

The 4-year average monthly precipitation of sulfur per acre in the rural districts of Alabama was lowest in September (0.47 pound) and highest in March (1.81 pounds). As a general rule, more sulfur was brought down during the winter, or wet, months than during the summer, or dry, months.

The data presented in this paper reveal that less sulfur is brought down in rural districts in Alabama than is reported in the literature for other rural regions of the nation. It is possible, however, that some of the data in the past was incorrect because of the use of faulty apparatus for collecting rain water. The walls of the container used for collecting rain water should be resistant to gaseous forms of atmospheric sulfur, otherwise the results will be abnormally high.

### EFFICIENCY OF ELEMENTAL SULFUR AND GYPSUM AS SOURCES OF SULFUR FOR GROWING COTTON

Ordinary mixed fertilizers of low analysis are usually well supplied with sulfur from superphosphate and ammonium sulfate, but sulfur in some form probably will need to be applied to soils if high-analysis fertilizers become common throughout the South.

The efficiency of elemental sulfur and gypsum as sources of sulfur was studied in the greenhouse. Cotton was grown in 2-gallon pots on five soils known to have received no sulfur in any commercial form for many years. Four sources of phosphorus and two sources of sulfur were compared with one another and with superphosphate (table 2). In order to eliminate the residual effect of the acid developed from the oxidation of the sulfur, only one crop was grown in each soil culture.

It will be noted that elemental sulfur increased the yields of plant material by 18.1 to 33.8 per cent when used with all four sources of nonsulfur-containing phosphates, but that in no case were the yields equal to those obtained with superphosphate; however, the superphosphate contained 57 per cent more sulfur than was added either in elemental form or as gypsum. Gypsum was about as efficient as elemental sulfur in increasing yields.

Sulfur applications markedly increased the percentages of $SO_3$ in the plant tissues. The increase due to elemental sulfur ranged from 94 to 160 per cent, depending on the sources of phosphorus used; and that due to gypsum ranged from 176 to 213 per cent. Superphosphate increased the concentration by 312 per cent. The apparent superiority of gypsum over elemental sulfur in increasing the sulfur content of the plants in this experiment was probably due to the fact that the elemental sulfur was not allowed sufficient time for oxidation before the crops were planted. A later experiment reported in this paper substantiates this conclusion.

In another greenhouse experiment, the same group of soils was used with $(NH_4)_2HPO_4$ as the only source of sulfur-free phosphorus (table 3). Lime was added in certain instances to neutralize the acidity developed by the sulfur and by the $(NH_4)_2HPO_4$. The 2-gallon pots of soil treated with sulfur were allowed

## TABLE 2

*Yields and SO₃ content of cotton plants grown in the greenhouse on soils treated with different kinds of fertilizer*

Results on dry-matter basis

| FERTILIZER TREATMENT* | NORFOLK SAND | | ORANGE-BURG LOAMY SAND | | NORFOLK SANDY LOAM | | ORANGE-BURG FINE SANDY LOAM | | NORFOLK LOAMY FINE SAND | | AVERAGE | | AVERAGE INCREASE IN YIELDS DUE TO SULFUR APPLIED | AVERAGE INCREASE IN S CONTENT OF TISSUE DUE TO SULFUR APPLIED |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Yield per A. | $SO_3$ | Yield per A. | $SO_2$ | Yield per A. | $SO_2$ | Yield per A. | $SO_3$ | Yield per A. | $SO_3$ | Yield per A. | $SO_3$ | | |
| | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | *per cent* | *per cent* |
| Triple superphosphate...... | 4218 | 0.17 | 3552 | 0.14 | 5328 | 0.16 | 5217 | 0.16 | 3552 | 0.17 | 4373 | 0.16 | | |
| Triple superphosphate and elemental sulfur†.. | 6216 | 0.35 | 4551 | 0.28 | 7104 | 0.32 | 5883 | 0.33 | 5439 | 0.36 | 5839 | 0.33 | 33.5 | 106.3 |
| Triple superphosphate and $CaSO_4 \cdot 2H_2O$‡... | 6327 | 0.52 | 5772 | 0.49 | 5994 | 0.48 | 5994 | 0.46 | 5772 | 0.55 | 5972 | 0.50 | 36.6 | 212.5 |
| Superphosphate§.. | 6105 | 0.73 | 6105 | 0.64 | 6216 | 0.65 | 6327 | 0.61 | 6216 | 0.66 | 6194 | 0.66 | 41.6 | 312.5 |
| $CaH_4(PO_4)_2$....... | 3996 | 0.15 | 2886 | 0.13 | 4773 | 0.17 | 5661 | 0.17 | 4662 | 0.16 | 4396 | 0.16 | | |
| $CaH_4(PO_4)_2$ and elemental S..... | 5883 | 0.33 | 5217 | 0.27 | 6549 | 0.31 | 5772 | 0.33 | 5994 | 0.33 | 5883 | 0.31 | 33.8 | 93.8 |
| $CzH_4(PO_4)_2$ and $CaSO_4 \cdot 2H_2O$.... | 6327 | 0.48 | 4884 | 0.47 | 6549 | 0.48 | 5994 | 0.42 | 6549 | 0.48 | 6061 | 0.47 | 37.9 | 193.8 |
| Slag............. | 5772 | 0.17 | 4107 | 0.13 | 4884 | 0.16 | 5550 | 0.16 | 4884 | 0.14 | 5039 | 0.15 | | |
| Slag and elemental S........ | 6105 | 0.44 | 5328 | 0.37 | 6438 | 0.36 | 6105 | 0.39 | 5772 | 0.40 | 5950 | 0.39 | 18.1 | 160.0 |
| Slag and $CaSO_4 \cdot 2H_2O$.... | 5772 | 0.50 | 5217 | 0.38 | 5994 | 0.48 | 6105 | 0.51 | 5772 | 0.47 | 5772 | 0.47 | 14.5 | 213.3 |
| $Na_2HPO_4$......... | 3885 | 0.20 | 2553 | 0.17 | 5328 | 0.15 | 5550 | 0.18 | 4329 | 0.15 | 4329 | 0.17 | | |
| $Na_2HPO_4$ and elemental S........ | 4662 | 0.38 | 4107 | 0.31 | 6771 | 0.34 | 5883 | 0.33 | 5994 | 0.34 | 5483 | 0.34 | 26.7 | 100.0 |
| $Na_2HPO_4$ and $CaSO_4 \cdot 2H_2O$.... | 4884 | 0.43 | 4218 | 0.54 | 6882 | 0.47 | 5994 | 0.41 | 5439 | 0.50 | 5483 | 0.47 | 26.7 | 176.5 |

* Adequate and equal amounts of P, K, N, Mg, and minor elements were supplied to all pots of soil in the form of nonsulfur-containing salts except for superphosphate as indicated. The complete plan was duplicated for five different soils, making a total of ten pots for each treatment.

† Applied in amounts equal to 200 pounds per acre of gypsum.

‡ 200 pounds per acre.

§ Applied at rate of 550 pounds per acre; contained S equivalent to 315 pounds of gypsum.

to stand at optimum moisture conditions for 6 months before being planted to peanuts, corn, turnips, soybeans, sorghum, and vetch. All crops were fertilized with adequate amounts of N, P, K, Mg, and minor elements.

The weight of the harvested crops indicates that lime applied without sulfur increased the yields of the various crops by an average of about 39 per cent but caused a slight decrease in the concentration of sulfur in the plant tissue. It is believed that this decrease was due to a deficiency of sulfur in the soil. Whenever sulfur or gypsum was applied, with or without lime, both the yields and the concentration of sulfur in the tissue were increased. (Sulfur in plant tissue was determined by oxidizing the tissue with sodium peroxide and precipitating the sulfur as $BaSO_4$.)

Elemental sulfur alone increased the average yields 81.4 per cent and the sulfur concentration in the plant tissue by an average of 385 per cent. When lime was added with the sulfur, the average yield was increased 132 per cent, and the concentration of sulfur in the plant was lower than without lime but was

TABLE 3

*Average yields and SO₃ contents of crops grown in the greenhouse on soils treated with different fertilizers\**

Results on dry-matter basis

| TREAT-MENT NUMBER† | SPECIAL FERTILIZER TREATMENT‡ | PEANUTS | | CORN | | TURNIPS | | SOY-BEANS | | SORGHUM | | VETCH | | AVERAGE | | INCREASE OVER TREATMENT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ | Yield per A. | SO₃ |
| | | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | lbs. | % | % | % |
| 1 | None | 8,836 | 0.23 | 4,063 | 0.08 | 155 | 0.28 | 4706 | 0.34 | 3774 | 0.10 | 1643 | 0.18 | 3863 | 0.20 | | |
| 2 | Lime | 9,124 | 0.21 | 5,950 | 0.09 | 1010 | 0.18 | 7170 | 0.26 | 6860 | 0.09 | 2153 | 0.19 | 5378 | 0.17 | 39.2 | −15.0 |
| 3 | Elemental S | 12,565 | 0.59 | 11,211 | 0.24 | 5816 | 1.29 | 5173 | 1.08 | 6305 | 0.44 | 977 | 2.21 | 7008 | 0.97 | 81.4 | 385.0 |
| 4 | CaSO₄·2H₂O | 13,387 | 0.51 | 11,766 | 0.22 | 5305 | 1.03 | 6394 | 0.78 | 6238 | 0.33 | 1132 | 1.87 | 7370 | 0.79 | 90.8 | 295.0 |
| 5 | S plus lime | 13,342 | 0.56 | 16,828 | 0.18 | 5128 | 1.03 | 8014 | 0.70 | 8059 | 0.31 | 2398 | 1.83 | 8962 | 0.77 | 132.0 | 285.0 |
| 6 | CaSO₄·2H₂O plus lime | 14,563 | 0.48 | 16,139 | 0.17 | 7015 | 0.77 | 8525 | 0.58 | 7792 | 0.23 | 9191 | 1.34 | 10,537 | 0.60 | 172.7 | 200.0 |
| 7 | Superphosphate plus lime | 13,065 | 0.36 | 13,564 | 0.10 | 6105 | 0.89 | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... |

\* The complete plan was duplicated for five different soils, making a total of 10 pots for each treatment.

† All treatments includes adequate fertilization with N, P, K, Mg, and minor elements.

‡ Lime was applied where indicated at rate of 1,000 pounds per acre; gypsum, at the rate of 200 pounds per acre; and sulfur, at a rate equivalent to 200 pounds of gypsum.

285 per cent above that in plants not receiving sulfur in the fertilizers. Gypsum was more efficient in increasing the yields than was elemental sulfur but not so efficient in raising the concentration of sulfur in the plant material.

In the experiment just described, only three crops were grown with superphosphate as the source of sulfur. Enough superphosphate was applied to supply sulfur equal to that applied in the elemental form or as gypsum, and the remainder of the phosphorus was applied as $(NH_4)_2HPO_4$. In these tests the sulfur in superphosphate was not superior to either elemental sulfur or gypsum.

It is interesting to note that peanuts, corn, and turnips showed large increases in yields as a result of sulfur fertilization; and that soybeans, sorghum, and vetch showed only small increases. On the other hand, peanuts and corn showed the smallest increases in the concentration of sulfur in the tissue, and vetch and

turnips showed the greatest increases as a result of sulfur fertilization. Some of the variations in the concentration of sulfur in the plant tissue were undoubtedly due to the variations in the amount of vegetative growth made by the different crops.

The sulfur concentration in the tissue of the plants not fertilized with sulfur varied between 0.08 and 0.34 per cent, but the same crops fertilized with sulfur varied from 0.17 to 2.21 per cent. Specifically, the addition of sulfur to the soil increased the concentration of sulfur in corn by about 120 per cent; in peanuts, 150 per cent; in soybeans, 200 per cent; in sorghum, 270 per cent; in turnips, 470 per cent; and in vetch, 1,000 per cent.

The increase in the concentration of sulfur in plant tissue should be of importance in animal nutrition.

### SUPPLEMENTS TO HIGH-ANALYSIS FERTILIZERS

Forty-five bins 14 by 31 feet were built on the agronomy farm, Auburn, Alabama, for this experiment. These bins consisted of concrete walls 2 feet high, set 18 inches into the ground at a slight slope to allow for slow surface runoff of water. Openings were made in the lower end walls of the bins to allow the excess surface rain water to escape and thereby prevent stagnation. Bins 1 to 30 were excavated to a depth of 18 inches and filled with well-composited Norfolk sandy loam obtained from an area not recently fertilized. Bins 31 to 45 contained the subsoil *in situ*, but before the walls were sunk, the surface soil of the area was mixed as thoroughly as possible by means of a slip scrape, disk, and harrow.

Corn and cotton were grown in all of the bins for 3 years prior to the experiment in an effort to settle the soil and to test the bins for uniformity of production. In 1931 and annually thereafter, fertilizers were applied as shown in table 4, and cotton was grown continuously for 9 years. Moderately good yields were obtained during the entire period. At the conclusion of the field work the soil in the bins was thoroughly sampled and analyzed for pH, exchangeable Ca, Mg, K, and H (table 4).

The high-analysis materials consisted of ammonium phoaphates, urea, and muriate of potash; and the low-analysis materials consisted of Chilean nitrate of soda and 16 per cent superphosphate. Supplements consisted of calcic lime, dolomite, gypsum, and a combination of the impurities found by analysis of 16 per cent superphosphate. Impurities other than those applied to plots 7 and 15 (table 4) are present in superphosphate, but only those listed in the table are considered in this study.

The exchangeable cations were extracted from the soil with normal ammonium acetate. Potassium was precipitated as the cobaltinitrite salt and titrated with permanganate; calcium was precipitated as the oxalate and titrated with permanganate; hydrogen was titrated with a standard alkali; and magnesium was determined colorimetrically by means of the 8-hydroxyquinoline microchemical technique.

## TABLE 4

*Yields of cotton and amounts of exchangeable cations and pH of soils treated with high-analysis fertilizers and various amendments*

| BIN NOS. | FERTILIZER TREATMENT* | SUPPLEMENTS ADDED TO THE SOIL† | pH OF SOIL 1939‡ | AV. YIELD OF SEED COTTON PER ACRE | | INCREASE IN YIELDS OF SEED COTTON DUE TO SUPPLEMENTS | | EXCHANGEABLE CATIONS PER 100 GM. SOIL AT CONCLUSION OF EXPERIMENT§ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1931–1935 | 1936–1939 | 1931–1935 | 1936–1939 | K | Ca | Mg | H | K, Ca, Mg |
| | | | | lbs. | lbs. | lbs. | lbs. | m.e. | me. | m.e. | m.e. | me. |
| 1, 9 | (NH₄)₂HPO₄-urea-KCl | None | 5.7 | 449 | 441 | ... | ... | .12 | 0.63 | .20 | 1.21 | 0.95 |
| 2, 10 | | CaCO₃ ⇌ to acidity | 6.4 | 678 | 792 | 229 | 351 | .11 | 1.01 | .13 | 0.87 | 1.25 |
| 3, 11 | | CaSO₄·2H₂O ⇌ to NH₄ | 6.0 | 887 | 919 | 438 | 478 | .11 | 0.79 | .08 | 1.07 | 0.98 |
| 4, 13 | | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ to NH₄ | 6.4 | 894 | 1025 | 445 | 584 | .11 | 1.28 | .14 | 0.84 | 1.53 |
| 5, 12 | No fertilizer | None | 5.9 | 189 | 177 | ... | ... | .08 | 0.97 | .13 | 0.74 | 1.18 |
| 6, 14 | (NH₄)₂HPO₄-urea-KCl | 1 ton CaCO₃ at start | 6.3 | 728 | 863 | 279 | 422 | .12 | 1.16 | .14 | 0.70 | 1.42 |
| 7, 15 | | CaCO₃ ⇌ to acidity; impurities ¶ | ... | 634 | 831 | 185 | 390 | ... | ... | ... | ... | ... |
| 8, 23 | Superphosphate-NaNO₃-KCl | None | 6.2 | 915 | 1166 | 466 | 725 | .13 | 1.23 | .17 | 0.77 | 1.53 |
| 16, 24 | NH₄H₂PO₄-urea-KCl | None | 5.8 | 557 | 486 | ... | ... | .12 | 0.75 | .10 | 0.94 | 0.97 |
| 17, 25 | | CaCO₃ ⇌ to acidity | 6.2 | 680 | 848 | 123 | 362 | .13 | 1.16 | .06 | 0.74 | 1.35 |
| 18, 26 | | CaSO₄·2H₂O ⇌ to NH₄ | 5.9 | 849 | 980 | 292 | 494 | .11 | 1.03 | .14 | 0.87 | 1.28 |
| 19, 28 | | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ to NH₄ | 6.4 | 804 | 932 | 247 | 446 | .10 | 1.31 | .12 | 0.75 | 1.53 |
| 20, 27 | No fertilizer | None | 5.8 | 174 | 146 | ... | ... | .07 | 0.68 | .09 | 0.70 | 0.84 |
| 21, 29 | NH₄H₂PO₄-urea-KCl | 1 ton CaCO₃ at start | 6.3 | 718 | 836 | 161 | 350 | .11 | 1.34 | .17 | 0.74 | 1.62 |
| 22, 30 | Superphosphate-urea-KCl | None | 6.0 | 829 | 1027 | 272 | 541 | .10 | 0.92 | .16 | 0.70 | 1.18 |
| 31, 38, 45 | No fertilizer | None | 6.4 | 386 | 283 | ... | ... | .08 | 1.13 | .19 | 0.46 | 1.40 |
| 32, 39 | NH₄H₂PO₄-urea-KCl | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ 2× NH₄ | 6.8 | 1029 | 1127 | 472 | 641 | .11 | 1.80 | .17 | 0.12 | 2.08 |
| 33, 40 | | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ to ½ NH₄ | 6.6 | 1014 | 1118 | 457 | 632 | .14 | 1.58 | .19 | 0.34 | 1.91 |
| 34, 41 | | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ to ¼ NH₄ | 6.6 | 976 | 1117 | 419 | 631 | .13 | 1.44 | .17 | 0.30 | 1.74 |
| 35, 42 | | CaCO₃ ⇌ to acidity; CaSO₄·2H₂O ⇌ to ⅛ NH₄ | 6.6 | 960 | 1130 | 403 | 644 | .12 | 1.54 | .19 | 0.66 | 1.85 |
| 36, 43 | | Dolomite ⇌ to acidity | 6.6 | 889 | 1070 | 332 | 584 | .15 | 1.34 | .29 | 0.74 | 1.78 |
| 37, 44 | | Dolomite ⇌ to acidity; CaSO₄·2H₂O ⇌ to ¼ NH₄ | 6.6 | 952 | 1232 | 395 | 746 | .10 | 1.49 | .30 | 0.80 | 1.89 |

* Base application of 600 pounds per acre 6–10–4 to all bins except 5, 12, 20, 27, 31, 38; and 45, which received no fertilizer.

† ⇌ means "equivalent to" the potential acidity of the fertilizer added or to the amount of ammonia nitrogen added in the fertilizer as indicated.

‡ Original pH of soil in bins 1 to 30 was 6.1, and in bins 31 to 44 it was 6.8, 1931.

§ Soil in bins 1 to 30 inclusive was obtained from a different location from that of soil in bins 31 to 44 inclusive. Soils were sampled to 8 inches in depth to obtain material for chemical analyses.

¶ Impurities in superphosphate added in following amounts per acre: 2 pounds $MgF_2$, 3 pounds $Fe_2O_3$, 7 pounds $Al_2F_6$, and 1.8 pounds $NaF$.

The results presented in table 4 suggest the following conclusions:

The increases in yields resulting from the addition of lime became greater with time.

Calcium sulfate produced greater increases in yield than did $CaCO_3$, but mixtures of $CaCO_3$ and $CaSO_4·2H_2O$ produced greater increases than either.

The exchangeable K content of the soil was about the same at the end of the experiment in all bins that received fertilizer, but the plots that received no fertilizer dropped considerably in exchangeable K.

Calcium carbonate was more efficient than $CaSO_4 \cdot 2H_2O$ in maintaining a supply of exchangeable Ca in the soil. The exchangeable Ca content of the soil that received high-analysis fertilizer without supplements was about half that of the soil that received supplements.

Dolomite nearly doubled the amount of exchangeable Mg in the soil.

The amount of exchangeable H was directly related to the pH of the soil. The amounts of lime added (amounts equivalent to the acidity of the fertilizers applied) caused a slight increase in the pH of the soil over the 9-year period. This indicates that the present methods of calculating the acidity and basicity of fertilizers is about correct.

It appears that enough sulfur was supplied for the maximum growth of cotton when $CaSO_4 \cdot 2H_2O$ was supplied in amounts equivalent to one eighth of the ammonia nitrogen added in the fertilizer. This might not be enough sulfur, however, if cotton yields were increased to a bale or more per acre.

Dolomite was superior to calcic lime as a supplement to high analysis fertilizer because of the magnesium it contained, but it was not superior as a neutralizer of acidity.

The yield of seed cotton was not increased by the addition of "impurities" ($MgF_2$, $Fe_2O_3$, $Al_2F_6$, and NaF) the first 5 years, but it was increased the last 4 years of the experiment.

Superphosphate and Chilean nitrate of soda produced distinct increases in yields as compared to those obtained with urea and ammonium phosphate. The increase is undoubtedly due to sodium, sulfur, magnesium, calcium, and probably some of the minor elements.

## SUMMARY

Experiments designed to test the need for supplementing high-analysis fertilizers with sulfur, calcium, magnesium, and minor elements showed the following results:

The amounts of sulfur brought down in rain in the rural districts in Alabama are small and are probably insufficient for the normal growth of common agricultural crops.

The efficiency of gypsum and elemental sulfur in increasing the yields of plant material differed but little.

The sulfur concentration of the plant tissue was increased more readily through the use of elemental sulfur as a supplement than through the use of gypsum. This was true only if the sulfur was given a chance to oxidize before a crop was planted.

Lime increased the yield of plant material but caused a decrease in the sulfur concentration in the tissue.

Sulfur, calcium, and magnesium in some form were necessary supplements to high-analysis fertilizers. Minor elements in low-grade materials also appeared to be important.

Lime was necessary was a supplement for neutralizing the acidity of high-analysis fertilizers in order to obtain maximum yields of crops. Lime added in amounts equivalent to the acidity of the fertilizer applied was sufficient to maintain the pH of the soil at a constant level

The concentration of any particular cation in the exchange material after 9

years of fertilization was higher in soils to which the cation was added than in in those to which it was not added.

In general, the use of high-analysis fertilizers relatively free of the usual impurities found in low-grade materials will hasten the development of nutritional problems involving calcium, magnesium, sulfur, acidity, and minor elements.

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# SOME EFFECTS OF FREEZING AND THAWING ON THE AGGREGATION AND PERMEABILITY OF DISPERSED SOILS[1]

ROBERT GARDNER[2]

*Colorado Agricultural Experiment Station*

The superficial effects of freezing and thawing on soil friability and on the disintegration of clods are well known to farmers and soil scientists. The more deeply seated effects of ice crystals on the integration of minute crystalline clay particles into compact aggregates, however, have received little attention from students of soil phenomena. This subject is of particular interest in connection with the restoration of structure to puddled soils or soils that have been dispersed as a result of sodium combined in the clay complex.

Salt accumulations in poorly drained soils frequently have a destructive effect on soil structure. This is particularly true where sodium salts predominate. The cohesive forces acting to maintain the soil constituents in granular aggregates are very weak when the replaceable cations consist mostly of sodium. They are particularly weak when the ratio of sodium to other cations is high and the total electrolyte content is low. After a soil has been subjected to a concentrated sodium salt solution and then leached to lower the concentration, the soil granules usually disintegrate. Concurrently with the disintegration of the soil granules in a wet soil, the clay changes to a fluid or semifluid state and the walls of the network of irregular pore spaces either collapse or change their configuration. Air becomes entrapped in many of the pore spaces, and this prevents their complete collapse; but under the surface tension of the moisture films, they tend to change from irregular connecting channels to discontinuous spherical cavities. The passages for air and water movement are sealed in this manner, and permeability is greatly reduced.

The problem of restoring saline soils to agricultural use frequently involves measures to restore soil structure after drains are installed to remove the excess salts. It has been shown[3] that merely removing the excess salts or removing the salts and replacing the exchangeable sodium with calcium may not restore the compact granular aggregates necessary for good structure. The crystalline clay particles when dispersed in water may be flocculated by calcium salts or other electrolytes, but the floccules tend to be very loosely packed aggregates in a semidispersed condition. Apparently the electrical forces causing flocculation are not able to bring the platy clay crystals into a compact arrangement unless supplemented by mechanical forces.

[3] Gardner, R. 1945 Some soil properties related to the sodium salt problems in irrigated soils. U. S. Dept. Agr. Tech. Bul. 902.

Two forces acting to supplement electrical flocculation in the formation of compact soil aggregates are those associated with drying and freezing. The favorable effect of drying is well recognized[4] and probably is due to the pressure of contracting moisture films on loosely packed aggregates. Little attention has been paid to the effect of ice crystals on the integration of loosely packed floccules or dispersed soil particles into compact aggregates. The phenomenon may be very important in the development of soil structure in cold climates and deserves more intensive study.

### EXPERIMENTAL

The effects of ice crystals on semidispersed soil and bentonite particles that had been flocculated from suspension in water by salt solutions and on soil samples treated with dry salts in the air-dry state and then leached with water have been investigated in this study. Samples of Fort Collins clay loam and bentonite from near Fort Collins were used in the experiments.

### Effect of freezing on semidispersed soil and bentonite

The bentonite and part of the soil used to make the suspensions were first treated with hydrochloric acid and washed with water to remove calcium carbonate. They were then dried and ground to pass through a 0.4 mm. sieve. The part of the soil not treated with acid was ground only to pass through a 2-mm. sieve. A mechanical analysis showed more than 75 per cent of the bentonite was less than $2\mu$ in size and about 33 per cent of the soil was below that limit.

Six 2-gm. samples of the acid-treated bentonite and six 5-gm. samples of acid-treated soil were moistened to approximately the lower plastic limit and were then worked in a mortar to break the aggregates. As the materials were worked, more water was added until the mass became fluid and well puddled. The samples were then brought into suspension in salt solutions with varying ratios of sodium and calcium sulfate and titrated with sodium and calcium hydroxides to a pH of approximately 7.5. The final normality of the solutions was between 0.02 and 0.05. The samples are numbered 1 to 6 in table 1.

Six other 2-gm. bentonite and six 5-gm. soil samples were washed twice with $2 N$ NaCl after the bentonite was neutralized with NaOH and were then dispersed by washing with water. They were next washed several times with $0.1 N$ solutions of $CaCl_2$ and NaCl in varying ratios and finally diluted to approximately $0.05 N$. The six samples of soil in this test had not been treated with acid because the acid-treated soil samples were found to be only slightly dispersed by the sodium salt treatments. The acid-treated bentonite samples, however, were as highly dispersed by the salt treatments as by mechanical puddling. The samples dispersed by sodium salt treatments are numbered 8 to 13 in table 1.

With the exception of the soil samples with a high percentage of sodium, the suspensions flocculated sufficiently to settle partly out of suspension, leaving

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[4] McGeorge, W. T., and Breazeale, J. F. 1938 Studies on soil structure: effect of puddled soil on plant growth. Ariz. Agr. Exp. Sta. Tech. Bul. 72.

clear solutions in the upper parts of the tubes. When the materials in suspension had settled to a constant apparent volume, the apparent volumes were recorded and the samples frozen. The frozen samples were then thawed and the apparent volumes recorded again. The samples were next agitated for 1 hour on a mechanical shaker, and the final apparent volumes were determined after the samples had been allowed to settle.

The results of the experiments to determine the effect of freezing on samples flocculated from suspension are shown in table 1 and figures 1 and 2. Figure 1 shows typical ice crystal patterns in flocculated bentonite, and figure 2 shows the flaky aggregates as they settled after the ice melted. Apparently, when the mass

TABLE 1

*Effect of freezing and thawing on the apparent specific gravity of flocculated soil and bentonite samples which previously had been dispersed by mechanical puddling or by sodium salts*

| | | APPARENT SPECIFIC GRAVITY | | | | | |
|---|---|---|---|---|---|---|---|
| | | Soil | | | Bentonite | | |
| NUMBER | Na:Ca | Before freezing | After freezing and thawing | After freezing, thawing, and shaking | Before freezing | After freezing and thawing | After freezing, thawing, and shaking |
| 1 | 5:0 | † | † | † | .03 | .12 | † |
| 2 | 4:1 | † | .66 | † | .05 | .15 | † |
| 3 | 3:2 | .43 | .81 | † | .10 | .37 | .18 |
| 4 | 2:3 | .48 | .93 | 0.96 | .10 | .40 | .20 |
| 5 | 1:4 | .46 | .78 | 0.96 | .10 | .40 | .40 |
| 6 | 0:5 | .32 | .94 | 0.96 | .10 | .40 | .40 |
| 7 | Untreated | .96 | .94 | 1.00 | .38 | .38 | .38 |
| 8 | 5:0 | .50 | .67 | † | .06 | .12 | † |
| 9 | 4:1 | .50 | .67 | 0.76 | .09 | .21 | .06 |
| 10 | 3:2 | .50 | .67 | 1.04 | .13 | .32 | .17 |
| 11 | 2:3 | .50 | .67 | 1.04 | .14 | .40 | .31 |
| 12 | 1:4 | .50 | .67 | 1.04 | .14 | .44 | .31 |
| 13 | 0:5 | .50 | .67 | 1.00 | .14 | .44 | .36 |

\* Samples 1 to 6 mechanically puddled; samples 8 to 13 dispersed by sodium salt treatment; sample 7 not dispersed.

† Did not flocculate completely but remained partly suspended in entire volume of liquid.

freezes, the loosely packed flocculated material offers little resistance to the natural development of ice crystals, which tend to develop in thin sheets. The soil or clay particles are forced into layers between the ice sheets as they form and become compressed and partly dehydrated between the crystal faces.

The stability of the flakes of soil or clay developed between the ice sheets depends to a large degree upon the type of cations in the system. The flakes of bentonite shown in the tube at the extreme right of figure 2 were only slightly broken as the ice melted. As the sodium percentage decreased the flakes became more distinct. The condition of the flakes in the soil samples was very similar to that of the flakes in the bentonite.

Table 1 shows the apparent specific gravity (apparent volume of soil divided by the dry weight of soil) of the samples before freezing, after freezing and thaw-
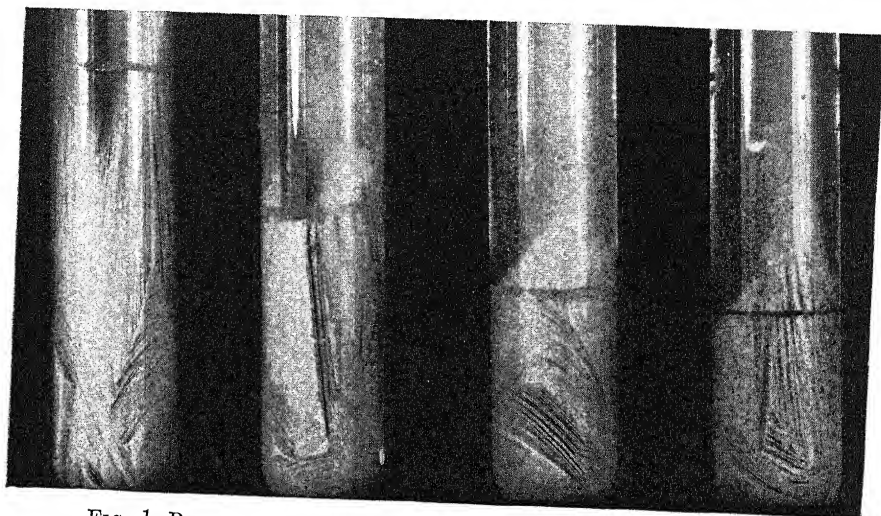


FIG. 1. PATTERNS OF FROST CRYSTALS IN FLOCCULATED BENTONITE
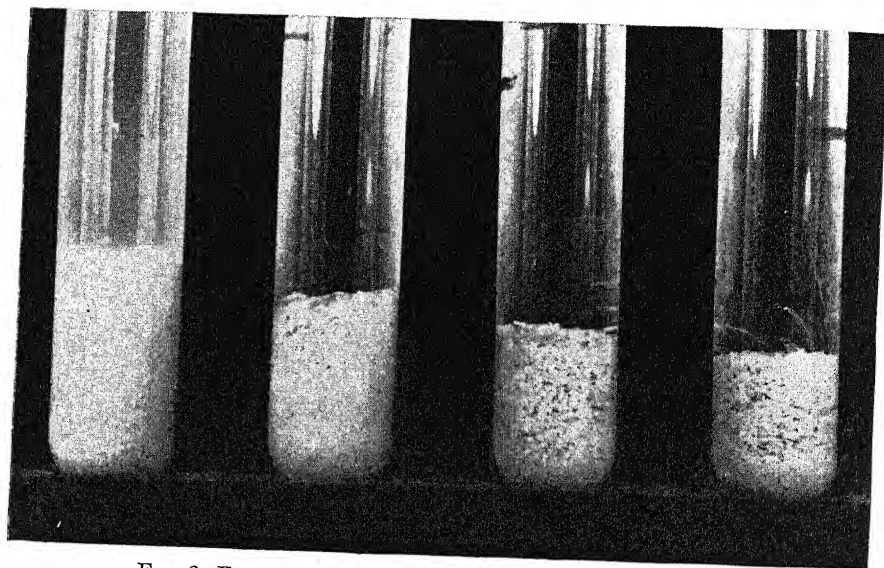


FIG. 2. FLAKY STRUCTURE OF BENTONITE AFTER FREEZING

Sodium percentage in solution Left to right—100, 80, 60, and 40; calcium percentage, 0, 20, 40, and 60

ing, and after agitation of the thawed samples on a mechanical shaker. The data show that the apparent specific gravity of the mass of flakes of the frozen and thawed samples was greatly increased as a result of freezing, which is evi-

dence that the density of the individual flakes was greater than that of the original floccules. The increase in the apparent specific gravity of the thawed samples was most pronounced in the samples with a high calcium percentage. The lower apparent specific gravity of samples with a high sodium percentage and less distinct flakes after thawing indicates a less stable condition of the aggregates. The lack of stability of the aggregates in the high sodium samples was made more evident by shaking the thawed samples. All the flakes were broken to a considerable extent by shaking, but the high apparent specific gravity after shaking of the high calcium samples indicated that small dense fragments still remained. The low apparent specific gravity of the high sodium samples was evidence that the crystals within the aggregates had become dispersed.

No pronounced difference was observed between the effects of freezing on soils which had been mechanically puddled and soils which had been dispersed by treatments with sodium salts when the ratios of sodium and calcium and the electrolyte concentration were comparable at the time of freezing. The evidence suggests that the primary effect of mechanical puddling is the disruption of the compact crystal aggregates and that the resulting physical state is essentially the same as that produced by a high sodium percentage and low total electrolyte content.

### Effect of freezing on permeability of dispersed soils

The previous experiments have shown that freezing is capable of producing comparatively stable soil aggregates from semidispersed soil material at very high moisture percentages. It cannot be concluded from the experiments, however, that the same effects would occur when more compact masses of soil are frozen under moisture conditions comparable to those prevailing in the field. A study of the effect of freezing on soils under the latter conditions was therefore undertaken.

In this experiment, 100-gm. samples of Fort Collins clay loam were each mixed with 2 gm. of sodium chloride and packed into glass extraction tubes 3 cm. by 12 cm. with an open stem at the bottom. The samples were then placed under a constant head of water and allowed to leach for several days. As leaching progressed, the upper portion of the soil column became dispersed before the moisture reached the bottom of the tubes. No percolate dripped from the samples, though the entire column eventually became wet. The upper half of the soil column, from which most of the salt had been leached, became lighter in color and the visible aggregates and irregular pore spaces disappeared leaving visible approximately spherical air pockets. These samples were then frozen several times, and though a network of connecting ice crystals was evident in the dispersed portion of the soil while frozen, the mass ran together upon thawing and remained impermeable.

Three grams of calcium chloride was then added to each tube and the water head maintained for 3 days. The soils still remained impermeable. After freezing and thawing, the channels made by the network of ice crystals remained

open and the permeability of the samples was restored. The ice crystal patterns were not so distinct in the more compact soil as in the samples shown in figure 1, but a distinct network of crystals was evident in the upper part of the tubes where the soil had been dispersed. In the lower part of the tubes, where the granules and irregular pore spaces had not been destroyed, no crystal patterns were evident. Apparently the ice formed in the pores or between the granules of the granular soil and had little effect on the structure.

The effect of freezing on the permeability of the soil samples is shown in table 2. The data in this table indicate that freezing of soils with a high sodium content and low total salts has little, if any, tendency to make the soils permeable, but that freezing after the addition of calcium salt to replace the sodium in the clay complex develops channels which are sufficiently stable to conduct

### TABLE 2

*Effect of freezing on soil permeability*

| SOIL TREATMENTS* | RATE OF WATER FLOW THROUGH SOIL UNDER UNIFORM HEAD | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Before freezing | After first freezing | After second freezing | After third freezing | After fourth freezing | After fifth freezing | After sixth freezing | After seventh freezing | After eighth freezing |
| | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* | *ml./hr.* |
| 1. Untreated soil packed dry.... | 17.1 | 32.5 | 54.4 | 36.3 | .... | .... | .... | .... | .... |
| 2. Puddled soil packed wet.... | 0.0 | 13.5 | 22.5 | 34.7 | .... | .... | .... | .... | .... |
| 3. Soil + 2 per cent NaCl packed dry.... | 0.0 | 0.0† | 25.5 | 44.3 | .... | .... | .... | .... | .... |
| 4. Soil + 2 per cent NaCl packed dry.... | 0.0 | 0.0 | 0.0 | 0.0 | 0.0† | 43.0 | 37.5 | 36.7 | 24.8 |

* All treatments in quadruplicate.

† 3 per cent CaCl₂ added before number of freezings indicated in column heading.

water, and the permeability is thus restored. Freezing had little effect on the permeability of the soil which had not been dispersed by sodium treatment or mechanical puddling.

The table also shows that soils made impermeable by mechanical puddling became permeable again after freezing.

### SUMMARY AND CONCLUSIONS

Experiments were conducted to determine the effect of freezing and thawing on the formation of aggregates and on permeability of dispersed soils. The following results were obtained:

Compaction and dehydration of semidispersed soils between the faces of adjacent ice crystals produced a stable flaky soil structure in soils with a high per-

EFFECTS OF FREEZING AND THAWING ON SOILS

centage of replaceable calcium and an unstable flaky soil structure in soils high in replaceable sodium.

Freezing and thawing did not restore permeability to impermeable sodium-saturated soils.

Replacing the sodium ions in sodium-saturated soils with calcium ions without freezing did not restore permeability, but freezing after calcium chloride was added to replace the sodium ions did restore permeability.

It is concluded that freezing and thawing may be utilized to good advantage in cold climates as aids in restoring structure and permeability in the process of reclaiming soils that have been injured by sodium salts.

# INFLUENCE OF THE ROOTSTOCK ON THE COMPOSITION OF CITRUS LEAVES AND ROOTLETS

A. R. C. HAAS

*University of California, Citrus Experiment Station*

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It was previously reported in this journal (5) that the amount of boron accumulated by citrus leaves was materially influenced by the rootstock variety. Leaves in any given orchard showed marked uniformity in the water-insoluble boron content of their dry matter. The relative order or type of boron accumulation in the leaves of seedling trees of different varieties was found to be the same as that impressed or imposed upon the leaves of the scion variety by these seedling varieties when used as rootstocks. For example, in seedling trees the leaves of the sour orange contained the least concentration of boron, whereas those of the trifoliate orange contained the most. This same relationship occurred also in the leaves of the scion variety when these same seedling variety roots were used. The nature of the cells of the particular rootstock variety was considered largely responsible for the boron-accumulating power of the leaves of the scion.

Eaton and Blair (3) after examining the analyses of leaves (of own-rooted sunflowers and artichokes or of Chinese box oranges and lemons) with respect to the accumulation of calcium, magnesium, sodium, potassium, or sulfate concluded that the analyses did not show sufficiently well marked differences in any of the determined ions to offer promise of significant differences in the reciprocally grafted plants.

The influence which rootstocks exert in the accumulation of boron in the leaves of the scion raises the question as to whether the rootstock effects are limited to boron or are operative in some degree on other nutrient elements. The present paper distinctly shows for the first time that the rootstock effects are not confined to the accumulation of boron, but that other elements may also be affected. It follows from this that the sampling of leaves of citrus trees in orchards for purposes of chemical analysis (2) might have greater significance if the rootstock varieties were taken into consideration. Thus the sampling of citrus trees in orchards would require not only a recognition of the rootstock but of the scion variety as well.

In relatively few orchards, however, is the true nature of the rootstock variety accurately known. Fortunately the determination of the rootstock is not limited to the nature of the bud union or to sprouts from the roots. A practical means of determining chemically whether the rootstock variety is sweet or sour orange was described by Halma and Haas (6) in 1929 and recently was used successfully by Halma, Smoyer, and Schwalm (7) in showing the marked susceptibility of sour orange rootstock to quick decline when budded with navel or Valencia orange scion varieties.

Although rootstock effects in lemon trees have merely been referred to in

this paper, it should be acknowledged that rootstocks may seriously affect the prevalence of lemon tree decline (1) and, as a result, greatly affect both the quality and the yield of fruit.

A disease known as the "Tristeza" disease of citrus (8) makes impossible in some countries the use of sour orange as a rootstock for orange trees. The various citrus rootstocks commonly used in orchards therefore have not only certain advantages but also certain limitations. In order to investigate some of the factors involved, it is necessary to study the chemical effects of the rootstocks on the nutrient accumulations in the scions. It is desirable to make comparisons of the composition of the leaves of seedling trees with that of the leaves of the scion variety budded on these seedling roots. When the material becomes available it will be desirable, furthermore, to make comparisons of the composition of the leaves of seedling trees (budded back on their own roots) with that of the leaves of the scion variety on these seedling roots. Data were obtained for the composition of the rootlets of several rootstock varieties in the Valencia orange rootstock plots at the Citrus Experiment Station at Riverside. In the present paper, not only are the various rootstock combinations dealt with (principally the leaves of Valencia orange scions) but also comparisons can be made with the leaves of some of these same varieties when grown as seedling trees, and with the rootlet composition of the rootstocks themselves.

## METHODS

The leaves were collected from two principal sources: the Valencia orange trees in the rootstock plots (field S 1), and the seedling orange trees and various scion-rootstock combinations in the pathology plots (field 12). Both fields are within one-fourth mile of each other at the Citrus Experiment Station, Riverside, California. The orchards are on Ramona loam soil.

The soil composition in the sampled plots was uniform, although variations may occur over more extensive areas. The soil fertilization in a given area also was uniform; this, however, does not preclude the temporary occurrence of local variableness in the soil as a result of such factors as absorption and irrigation. It is recognized that differences in composition of the soil with respect to the ions can influence the chemical composition of the above- and below-ground parts of citrus trees. In the experimental orchards studied, the roots of trees of one plot could be in competition with those of trees of other plots. When the scions were similar, the rootstocks in such plots had the opportunity of competing with other rootstocks as well as with one another. Although the rootstocks are shown in this paper as influencing in certain respects the composition of the scion, it is understood that other factors such as fertilization, irrigation, light, and temperature also may affect the scion composition in varying degrees. The deciduous nature of trifoliate orange (seedling) trees when unbudded adds still another factor.

The leaves collected were fully mature in every case and free of mottle leaf (zinc-deficiency) symptoms. The leaves were washed individually in running distilled water and at once were wiped dry. After being dried in a well-venti-

lated oven at 65°C., they were finely ground in a Wiley mill. The samples were then placed in envelopes made by folding heavy brown wrapping paper, and each envelope was then inserted into a heavy paper mail bag bearing the data descriptive of the contained sample. The samples were stored in an oven maintained at about 50°C. and were removed only temporarily for the weighing of duplicate samples.

Cover crops are ordinarily planted in the rootstock orchard in autumn and in order not to confuse other rootlets with those of citrus, the latter were collected while the orchard was still free of other plants. Several rootlet samples to the depth of a shovel were collected from each of the trees in each of the selected plots. The large freshly collected samples of rootlets with adhering soil were brought at once into the laboratory, where the rootlets one-eighth inch or less thick were selected. Each mass of rootlets was washed like a sponge 20 to 25 times in new lots of tap water in large glass jars, and this was followed by similar washings with distilled water. Most of the moisture was then shaken away, and the samples were rapidly dried in a large ventilated oven maintained at 65°C. When dry, the large samples were ground in a Wiley mill and were stored in a manner previously described for leaves.

The water-soluble and insoluble fractions were obtained in the following manner: The weighed sample of dry matter was placed in a beaker (150-ml. capacity) to which was then added about 100 ml. of distilled water. The suspension was stirred frequently and was filtered after standing about 6 hours. A perforated palladium cone was used to support the filter paper (Whatman No. 42) during the filtration, in which vacuum suction was employed. The filtrate was caught in a beaker placed inside a glass bell jar, the suction being applied at a tubulature near the base of the jar. The contents of the original beaker were transferred to the filter paper in the funnel inserted through a rubber stopper in the top of the jar. Washing of the contents of the filter paper was continued until about 400 ml. of filtrate was obtained from an original 5-gm. sample of dry matter. Silica (Vitreosil) casseroles with side arms removed were used for evaporating the filtrate (water-soluble fraction) and for drying the filter paper and its residue (water-insoluble fraction).

Ignition was carried on at low heat with Fisher burners in which the air vents were almost closed. When the dishes were cool, the soluble salts were extracted with distilled water, and filtration was made into a volumetric flask. After being washed with hot distilled water, the filter paper and residue were returned to the original dish, dried, and reignited. This process was repeated until the ash was free of carbon after an ignition (usually two or three ignitions were adequate). Dilute HCl was added to the ash in the cooled dish, and solution was aided by then heating the contents of the dish, after which the filtration and making to volume (usually 100 ml.) with distilled water was completed.

Calcium was determined in suitable aliquots by the titration of the oxalate with $KMnO_4$; magnesium was weighed as $Mg_2P_2O_7$; potassium was weighed as the chlorplatinate; phosphorus was determined colorimetrically as the molybdenum blue compound after the ignition of the dry matter with magnesium nitrate

followed by solution of the residue with $HNO_3$, filtering, and making to volume (usually 1 gm. dry matter, a final volume of 100 ml., and an aliquot of 1 ml. were used). In a parallel set of phosphorus determinations, $H_2SO_4$ was used in place of $HNO_3$ with no obvious advantage. Color development in the determination of phosphorus was accomplished by shaking the color flask 1 minute by hand, followed by placing the flask for 7 minutes in a water bath at 20°C. and then shaking the flask prior to determining the scale A (logarithm of light transmission) reading in a Fisher electrophotometer.

Total nitrogen (including nitrates) was determined by digestion with a mixture of $H_2SO_4$ and salicylic acid and the later addition of a mixture of the sulfates of K, Fe, and Cu, followed by distillation of the ammonia into boric acid and titration with a mixed indicator (bromcresol green and methyl red). Though sodium was estimated by means of the zinc uranyl acetate, the amounts were very small and of no consequence otherwise. Total sulfur was determined by the ignition of the dry matter in the presence of magnesium nitrate and

TABLE 1

*Water-solubility of calcium, magnesium, and potassium in the dry matter of leaves collected April 5, 1943, in C.E.S. Path. Plot, field 12*

| SCION VARIETY | CALCIUM IN DRY MATTER OF LEAVES | | | MAGNESIUM IN DRY MATTER OF LEAVES | | | POTASSIUM IN DRY MATTER OF LEAVES | | |
|---|---|---|---|---|---|---|---|---|---|
| | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total |
| | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Navel orange............... | 2.45 | 2.57 | 5.02 | .247 | .014 | .261 | .712 | .090 | .802 |
| Eureka lemon............... | 1.14 | 4.50 | 5.64 | .295 | .063 | .358 | .551 | .079 | .630 |
| Marsh grapefruit........... | 1.73 | 3.12 | 4.85 | .251 | .037 | .288 | .667 | .073 | .740 |

weighing the sulfate as barium sulfate. The use of concentrated $HNO_3$ instead of magnesium nitrate for ignition in the total sulfur determination was found to give unsatisfactory results. Sugars were determined by the iodate-iodide method using sodium thiosulfate. When the results for a given element or substance were obtained, the data were arranged in such a way as to show whether the rootstock had any effect.

### RESULTS WITH CITRUS LEAVES

#### Calcium

Citrus leaves are especially rich in calcium. Without considering the rootstock, Haas (4) showed that nearly 50 per cent of the total calcium in the dry matter of mature orange leaves is water-soluble and that only about 20 per cent of the calcium in the dry matter of mature lemon leaves is water-soluble. This is also shown in table 1, in which collections of leaves were made without regard to rootstock. The dry matter of the grapefruit leaves in table 1 contained about 35 per cent of soluble calcium, that of the orange leaves about 49 per cent and that of the lemon leaves about 20 per cent.

If we now consider the influence of the rootstock (table 2) on the calcium in grapefruit leaves, we find that the leaves of trees on sour orange rootstock

## TABLE 2

*Composition of mature citrus leaves as affected by sweet orange and sour orange rootstocks*

| SCION / ROOTSTOCK | DATE OF COLLECTION | LOCATION IN C.E.S. PATH. PLOT | | CALCIUM IN DRY MATTER | | | MAGNESIUM IN DRY MATTER | | | POTASSIUM IN DRY MATTER | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Row | Tree | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total |
| | 1930 | | | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent |
| Marsh grapefruit / Sweet orange | Oct. 3 | 18 | 2 | 1.63 | 3.38 | 5.01 | .374 | .078 | .452 | 1.273 | .063 | 1.336 |
| Marsh grapefruit / Sour orange | Oct. 3 | 18 | 6 | 2.75 | 3.45 | 6.20 | .534 | .081 | .615 | 0.652 | .092 | 0.744 |
| Marsh grapefruit / Sweet orange | Dec. 11 | 18 | 3 | 2.64 | 3.11 | 5.75 | .380 | .051 | .431 | 1.191 | .051 | 1.242 |
| Marsh grapefruit / Sour orange | Dec. 11 | 18 | 7 | 3.01 | 3.38 | 6.39 | .485 | .074 | .559 | 0.495 | .039 | 0.534 |
| Eureka lemon / Sweet orange | Oct. 3 | 30 | 6 | 1.60 | 5.95 | 7.55 | .448 | .080 | .528 | 0.846 | .067 | 0.913 |
| Eureka lemon / Sour orange | Oct. 3 | 30 | 2 | 1.64 | 5.68 | 7.32 | .395 | .074 | .469 | 0.874 | .060 | 0.934 |
| Eureka lemon / Sweet orange | Dec. 11 | 30 | 7 | 1.65 | 5.84 | 7.49 | .451 | .054 | .505 | 0.648 | .078 | 0.726 |
| Eureka lemon / Sour orange | Dec. 11 | 30 | 3 | 1.79 | 5.37 | 7.16 | .371 | .069 | .440 | 0.656 | .056 | 0.712 |
| Navel orange / Sweet orange | Oct. 3 | 13 | 1,2 | 1.57 | 2.34 | 3.91 | .251 | .057 | .308 | 1.701 | .050 | 1.751 |
| Navel orange / Sour orange | Oct. 3 | 6 | 1,2,4 | 2.76 | 3.17 | 5.93 | .301 | .049 | .350 | 1.207 | .046 | 1.253 |
| Navel orange / Sweet orange | Dec. 11 | 13 | 3,4 | 2.07 | 2.33 | 4.40 | .268 | .044 | .312 | 1.672 | .032 | 1.704 |
| Navel orange / Sour orange | Dec. 11 | 6 | 5,6,7 | 2.37 | 2.66 | 5.03 | .317 | .067 | .384 | 1.402 | .047 | 1.449 |

contain more soluble and total calcium and possibly more insoluble calcium than do the leaves of trees on sweet orange rootstocks. This is also true for

navel orange leaves on these stocks.   Lemon leaves failed to show such a difference, although data for additional samples are much to be desired.

In table 3 the data for calcium in the dry matter of the leaves of Valencia orange grown on various rootstocks are arranged in descending order of the soluble calcium.   Examination of these data reveals that the sweet orange

### TABLE 3

*Relation of rootstock variety to calcium content of mature Valencia orange leaves*

| ROOTSTOCK VARIETY | LOCATION IN ORCHARD (C.E.S. FIELD S 1) | | | CALCIUM IN DRY MATTER | | |
|---|---|---|---|---|---|---|
| | Block | Row | Trees | Water-soluble | Water-insoluble | Total |
| | | | | *per cent* | *per cent* | *per cent* |
| Siamese shaddock............. | A | 35 | 11–15 | 3.40 | 3.24 | 6.64 |
| Trifoliate orange............. | A | 21 | 1–5 | 3.36 | 3.59 | 6.95 |
| Trifoliate orange............. | B | 18 | 11–15 | 3.21 | 3.17 | 6.38 |
| African sour orange......... | A | 30 | 11–15 | 3.19 | 3.21 | 6.40 |
| Cleopatra mandarin......... | A | 31 | 11–15 | 3.17 | 2.94 | 6.11 |
| Cleopatra mandarin......... | A | 32 | 11–15 | 3.15 | 3.13 | 6.28 |
| Trifoliate orange............. | C | 20 | 1–5 | 3.12 | 3.05 | 6.17 |
| Savage citrange.............. | A | 23 | 6–10 | 3.11 | 3.36 | 6.47 |
| Brazilian sour orange........ | A | 29 | 11–15 | 3.05 | 3.21 | 6.26 |
| Brazilian sour orange........ | A | 29 | 1–5 | 3.01 | 3.06 | 6.07 |
| Savage citrange.............. | A | 22 | 1,2,4,5 | 2.97 | 3.57 | 6.54 |
| Rubidoux sour orange........ | A | 33 | 6–10 | 2.94 | 3.37 | 6.31 |
| Trifoliate orange............. | A | 27 | 11–15 | 2.90 | 3.17 | 6.07 |
| Duncan grapefruit............ | A | 34 | 11–15 | 2.90 | 3.28 | 6.18 |
| Duncan grapefruit............ | A | 31 | 1–5 | 2.90 | 3.02 | 5.92 |
| Siamese shaddock............. | A | 32 | 1–5 | 2.89 | 3.13 | 6.02 |
| Trifoliate orange............. | A | 22 | 6–10 | 2.87 | 3.12 | 5.99 |
| C.E.S. 343 grapefruit......... | A | 36 | 11–15 | 2.86 | 2.98 | 5.84 |
| Rubidoux sour orange........ | A | 28 | 1–5 | 2.81 | 3.27 | 6.08 |
| C.E.S. 362 sweet orange...... | A | 29 | 6–10 | 2.78 | 2.93 | 5.71 |
| Sampson tangelo............. | A | 30 | 6–10 | 2.72 | 2.93 | 5.65 |
| Lemon shaddock.............. | A | 33 | 11–13 | 2.71 | 2.85 | 5.56 |
| African sour orange.......... | A | 27 | 1–5 | 2.66 | 2.99 | 5.65 |
| Rough lemon................. | A | 32 | 6–10 | 2.64 | 2.60 | 5.24 |
| Rough lemon................. | A | 30 | 1–5 | 2.61 | 2.59 | 5.20 |
| Koethen sweet orange........ | A | 28 | 6–10 | 2.51 | 2.79 | 5.30 |
| Sampson tangelo............. | A | 31 | 6–10 | 2.40 | 2.94 | 5.34 |
| C.E.S. 343 grapefruit......... | A | 33 | 1–5 | 2.39 | 2.89 | 5.28 |
| C.E.S. 362 sweet orange...... | A | 36 | 1–5 | 2.37 | 2.78 | 5.15 |
| Koethen sweet orange........ | A | 35 | 1–5 | 2.07 | 2.50 | 4.57 |

rootstocks occur in the lower part of the list, whereas the sour oranges, except for one of the African samples, occur in the upper part.   Cleopatra mandarin, Brazilian sour orange, Duncan grapefruit, and rough lemon rootstocks are of interest because of the close agreement of the values obtained for soluble calcium in the Valencia orange leaves of trees on a given variety.   The trees on Duncan grapefruit were three rows apart and in different portions of the rows.   Thus

the percentage of calcium in Valencia orange leaves, though differing considerably in certain cases in the same orchard, is closely related to the identity of the rootstock.

The data (table 4) for calcium in the dry matter of leaves of large seedling trees show that the leaves of sour orange contain more calcium (soluble, insoluble, and total) than those of sweet orange. In this respect the type of calcium accumulation which these roots of seedling trees impress upon their own leaves is of the same order or type as that which these same roots impress upon the leaves of any orange or grapefruit scion budded on them. One difference in the accumulation of calcium in the leaves of seedling trees and in Valencia orange leaves of trees on sweet, sour, and trifoliate orange rootstocks lies in the relationship between the water-soluble and the water-insoluble calcium. In the dry matter of the leaves of seedling trees the ratio was roughly 1:2 (table 4),

TABLE 4

*Water-solubility of calcium, magnesium, and potassium, and the total phosphorus content in mature leaves\* of seedling citrus trees*

| SEEDLING VARIETY | LOCATION IN C.E.S. PATH. PLOT | | CALCIUM IN DRY MATTER | | | MAGNESIUM IN DRY MATTER | | | POTASSIUM IN DRY MATTER | | | TOTAL PHOSPHORUS IN DRY MATTER |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Row | Trees | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total | Water-soluble | Water-insoluble | Total | |
| | | | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* | *per cent* |
| Trifoliate orange...... | 25 | 9–13 | 1.73 | 2.55 | 4.28 | .308 | .057 | .365 | 0.870 | .047 | 0.917 | .177 |
| Sour orange (Beladi) Tunis.............. | 21 | 21–23 | 1.56 | 3.65 | 5.21 | .296 | .055 | .351 | 0.521 | .056 | 0.577 | .092 |
| Sour orange (Sicily)... | 20 | 23,24 | 1.75 | 4.01 | 5.76 | .291 | .048 | .339 | 0.595 | .052 | 0.647 | .107 |
| Sweet orange......... | 31 | 4,8 | 1.38 | 2.55 | 3.93 | .213 | .060 | .273 | 1.272 | .074 | 1.346 | .145 |

\* Leaves collected June 26, 1943.

whereas in that of the Valencia orange leaves on various rootstocks, the ratio was roughly 1:1 (table 3).

## Magnesium

As shown in table 1, where the rootstocks are unknown, the lemon leaves contain more magnesium than the orange leaves. With grapefruit and navel orange scions, the leaves in table 2 contain more soluble and total magnesium when collected from trees on sour orange than on sweet orange rootstocks, whereas the reverse appears to be true when lemon scions are used. The magnesium and calcium values show the same relationship (table 2) as regards grapefruit and orange leaves.

In table 5 the rootstocks are arranged in descending order of the soluble magnesium in the dry matter of the leaves of Valencia orange grown on them. Much of the magnesium in the orange leaves is water-soluble. Shaddock,

trifoliate orange, rough lemon, and Cleopatra mandarin are relatively high in the list; all of the grapefruit rootstocks are at the bottom; and there is a suggestion that the sour orange rootstocks are above the sweet orange.   There is also the possibility that various sour orange rootstocks differ in their effect on soluble

## TABLE 5

*Relation of rootstock variety to magnesium content of mature Valencia orange leaves*

| ROOTSTOCK VARIETY | LOCATION IN ORCHARD (C.E.S. FIELD S 1) | | | MAGNESIUM IN DRY MATTER | | |
|---|---|---|---|---|---|---|
| | Block | Row | Trees | Water-soluble | Water-insoluble | Total |
| | | | | *per cent* | *per cent* | *per cent* |
| Lemon shaddock............ | A | 33 | 11–13 | .451 | .060 | .511 |
| Siamese shaddock........... | A | 35 | 11–15 | .440 | .037 | .477 |
| Trifoliate orange............ | B | 18 | 11–15 | .422 | .043 | .465 |
| Siamese shaddock........... | A | 32 | 1–5 | .404 | .050 | .454 |
| Trifoliate orange............ | A | 27 | 11–15 | .392 | .056 | .448 |
| Rough lemon................ | A | 32 | 6–10 | .387 | .042 | .429 |
| Trifoliate orange............ | C | 20 | 1–5 | .382 | .058 | .440 |
| Trifoliate orange............ | A | 22 | 6–10 | .371 | .042 | .413 |
| Trifoliate orange............ | A | 21 | 1–5 | .368 | .028 | .396 |
| Sampson tangelo............ | A | 30 | 6–10 | .354 | .047 | .401 |
| Cleopatra mandarin.......... | A | 31 | 11–15 | .347 | .052 | .399 |
| African sour orange.......... | A | 30 | 11–15 | .345 | .046 | .391 |
| Rough lemon................ | A | 30 | 1–5 | .344 | .049 | .393 |
| Cleopatra mandarin.......... | A | 32 | 11–15 | .343 | .046 | .389 |
| Savage citrange............. | A | 23 | 6–10 | .332 | .045 | .377 |
| Brazilian sour orange......... | A | 29 | 11–15 | .330 | .044 | .374 |
| African sour orange.......... | A | 27 | 1–5 | .328 | .040 | .368 |
| Brazilian sour orange......... | A | 29 | 1–5 | .317 | .033 | .350 |
| C.E.S. 362 sweet orange...... | A | 36 | 1–5 | .317 | .051 | .368 |
| C.E.S. 362 sweet orange...... | A | 29 | 6–10 | .308 | .030 | .338 |
| Sampson tangelo............ | A | 31 | 6–10 | .304 | .044 | .348 |
| Rubidoux sour orange........ | A | 33 | 6–10 | .303 | .049 | .352 |
| Savage citrange............. | A | 22 | 1,2,4,5 | .298 | .084 | .382 |
| Koethen sweet orange........ | A | 28 | 6–10 | .295 | .036 | .331 |
| Rubidoux sour orange........ | A | 28 | 1–5 | .290 | .067 | .357 |
| C.E.S. 343 grapefruit........ | A | 33 | 1–5 | .281 | .045 | .326 |
| Koethen sweet orange........ | A | 35 | 1–5 | .270 | .048 | .318 |
| Duncan grapefruit........... | A | 34 | 11–15 | .260 | .027 | .287 |
| C.E.S. 343 grapefruit........ | A | 36 | 11–15 | .258 | .041 | .299 |
| Duncan grapefruit........... | A | 31 | 1–5 | .253 | .036 | .289 |

magnesium.   The variations in the magnesium content of the leaves with various rootstocks again emphasize the need of knowing the rootstock variety when collecting leaves for chemical analysis.

In leaves of seedling trees (table 4) the trifoliate orange heads the list for soluble and total magnesium, followed by sour orange and then sweet orange.

The data for seedling trees appear to be good criteria of the effects of these roots on other tops budded upon them.

### Potassium

Where the rootstocks are unknown (table 1), the lemon leaves contain the least potassium and the orange leaves the most. The data in table 2 show that the soluble and the total potassium in grapefruit and navel orange leaves are

TABLE 6

*Relation of rootstock variety to potassium content of mature Valencia orange leaves*

| ROOTSTOCK VARIETY | LOCATION IN ORCHARD (C.E.S. FIELD S 1) | | | POTASSIUM IN DRY MATTER | | |
|---|---|---|---|---|---|---|
| | Block | Row | Trees | Water-soluble | Water-insoluble | Total |
| | | | | *per cent* | *per cent* | *per cent* |
| Koethen sweet orange........ | A | 35 | 1–5 | .908 | .050 | .958 |
| Sampson tangelo............. | A | 30 | 6–10 | .888 | .047 | .935 |
| Duncan grapefruit........... | A | 31 | 1–5 | .876 | .046 | .922 |
| Sampson tangelo............. | A | 31 | 6–10 | .853 | .057 | .910 |
| C.E.S. 343 grapefruit........ | A | 33 | 1–5 | .829 | .059 | .888 |
| Duncan grapefruit........... | A | 34 | 11–15 | .732 | .055 | .787 |
| Trifoliate orange............ | A | 27 | 11–15 | .732 | .090 | .822 |
| Trifoliate orange............ | A | 22 | 6–10 | .705 | .063 | .768 |
| Siamese shaddock........... | A | 32 | 1–5 | .660 | .047 | .707 |
| C.E.S. 343 grapefruit........ | A | 36 | 11–15 | .644 | .076 | .720 |
| Koethen sweet orange........ | A | 28 | 6–10 | .638 | .055 | .693 |
| C.E.S. 362 sweet orange...... | A | 29 | 6–10 | .638 | .056 | .694 |
| C.E.S. 362 sweet orange...... | A | 36 | 1–5 | .633 | .053 | .686 |
| Brazilian sour orange........ | A | 29 | 1–5 | .604 | .050 | .654 |
| Trifoliate orange............ | C | 20 | 1–5 | .596 | .068 | .664 |
| Savage citrange............. | A | 22 | 1,2,4,5 | .590 | .093 | .683 |
| Cleopatra mandarin......... | A | 31 | 11–15 | .578 | .065 | .643 |
| Savage citrange............. | A | 23 | 6–10 | .578 | .056 | .634 |
| Lemon shaddock............. | A | 33 | 11–13 | .578 | .057 | .635 |
| African sour orange......... | A | 27 | 1–5 | .574 | .018 | .592 |
| Rubidoux sour orange........ | A | 28 | 1–5 | .567 | .047 | .614 |
| Trifoliate orange............ | B | 18 | 11–15 | .566 | .057 | .623 |
| Cleopatra mandarin.......... | A | 32 | 11–15 | .555 | .048 | .603 |
| Rough lemon................ | A | 30 | 1–5 | .553 | .044 | .597 |
| Rubidoux sour orange........ | A | 33 | 6–10 | .531 | .058 | .589 |
| Siamese shaddock........... | A | 35 | 11–15 | .529 | .061 | .590 |
| Trifoliate orange............ | A | 21 | 1–5 | .520 | .050 | .570 |
| Brazilian sour orange........ | A | 29 | 11–15 | .519 | .074 | .593 |
| Rough lemon................ | A | 32 | 6–10 | .514 | .059 | .573 |
| African sour orange......... | A | 30 | 11–15 | .500 | .065 | .565 |

greater when sweet orange rather than sour orange rootstocks are used. The leaves of grapefruit trees on sweet orange rootstocks contained about double the potassium concentration of those on sour orange rootstocks. The inverse relation of calcium and potassium can be seen in the data of table 2 for grape-

fruit and orange leaves. The rootstocks showed no appreciable effect on potassium in the lemon leaves.

The high potassium content of navel orange leaves from trees on sweet orange rootstock is confirmed by the data in table 6, in which various rootstocks on which Valencia orange trees were grown are arranged in descending order of

TABLE 7

*Total nitrogen in mature valencia orange leaves collected from trees on various rootstocks*

| ROOTSTOCK VARIETY | LOCATION IN ORCHARD (C.E.S. FIELD S 1) | | | TOTAL NITROGEN IN DRY MATTER |
|---|---|---|---|---|
| | Block | Row | Trees | |
| | | | | *per cent* |
| Koethen sweet orange......... | A | 35 | 1–5 | 2.73 |
| Koethen sweet orange......... | A | 28 | 6–10 | 2.45 |
| Rough lemon.................. | A | 32 | 6–10 | 2.43 |
| Duncan grapefruit............ | A | 31 | 1–5 | 2.41 |
| African sour orange.......... | A | 27 | 1–5 | 2.41 |
| C.E.S. 362 sweet orange....... | A | 36 | 1–5 | 2.41 |
| C.E.S. 343 grapefruit......... | A | 33 | 1–5 | 2.40 |
| Lemon shaddock.............. | A | 33 | 11–13 | 2.40 |
| Duncan grapefruit............ | A | 34 | 11–15 | 2.38 |
| Sampson tangelo.............. | A | 30 | 6–10 | 2.35 |
| Sampson tangelo.............. | A | 31 | 6–10 | 2.34 |
| Rough lemon................. | A | 30 | 1–5 | 2.34 |
| Trifoliate orange............. | C | 20 | 1–5 | 2.32 |
| Brazilian sour orange......... | A | 29 | 1–5 | 2.31 |
| C.E.S. 343 grapefruit......... | A | 36 | 11–15 | 2.31 |
| C.E.S. 362 sweet orange....... | A | 29 | 6–10 | 2.30 |
| Cleopatra mandarin........... | A | 31 | 11–15 | 2.27 |
| Trifoliate orange............. | A | 27 | 11–15 | 2.27 |
| Trifoliate orange............. | A | 22 | 6–10 | 2.26 |
| Siamese shaddock............. | A | 32 | 1–5 | 2.25 |
| Brazilian sour orange......... | A | 29 | 11–15 | 2.25 |
| Rubidoux sour orange........ | A | 28 | 1–5 | 2.25 |
| Savage citrange.............. | A | 23 | 6–10 | 2.25 |
| Siamese shaddock............. | A | 35 | 11–15 | 2.23 |
| Cleopatra mandarin........... | A | 32 | 11–15 | 2.22 |
| Savage citrange.............. | A | 22 | 1,2,4,5 | 2.10 |
| Rubidoux sour orange........ | A | 33 | 6–10 | 2.08 |
| Trifoliate orange............. | B | 18 | 11–15 | 2.07 |
| African sour orange.......... | A | 30 | 11–15 | 2.07 |
| Trifoliate orange............. | A | 21 | 1–5 | 2.01 |

the soluble potassium in the leaves. In the upper 13 rootstocks listed, are found all the sweet orange but none of the sour orange varieties. The trifoliate orange is variable. All of the tangelo and grapefruit varieties are in the upper 13 rootstocks. Expansion of table 6 to include frequent leaf samplings and a number of soil types might add materially to the value of such a list. Recognition of the influence of the rootstock variety upon nutrient accumulation in-

creases the value of studies in which leaf analysis is used in diagnosing the fertility needs of citrus trees (2).

Table 4 shows the high potassium content of the leaves of large sweet orange seedling trees and the very low (about 50 per cent as much) potassium content of the leaves of large sour orange seedling trees.

TABLE 8

*Total sulfur in mature valencia orange leaves collected from trees on various rootstocks*

| ROOTSTOCK VARIETY | LOCATION IN ORCHARD (C.E.S. FIELD S 1) | | | TOTAL SULFUR IN DRY MATTER |
|---|---|---|---|---|
| | Block | Row | Trees | |
| | | | | *per cent* |
| Rough lemon................. | A | 30 | 1–5 | .319 |
| C.E.S. 343 grapefruit......... | A | 33 | 1–5 | .314 |
| Duncan grapefruit............ | A | 34 | 11–15 | .312 |
| Rough lemon................. | A | 32 | 6–10 | .311 |
| Duncan grapefruit............ | A | 31 | 1–5 | .311 |
| Savage citrange.............. | A | 22 | 1,2,4,5 | .310 |
| C.E.S. 362 sweet orange....... | A | 36 | 1–5 | .309 |
| Siamese shaddock............ | A | 35 | 11–15 | .308 |
| Savage citrange.............. | A | 23 | 6–10 | .295 |
| C.E.S. 343 grapefruit......... | A | 36 | 11–15 | .290 |
| Koethen sweet orange......... | A | 35 | 1–5 | .284 |
| Koethen sweet orange......... | A | 28 | 6–10 | .281 |
| African sour orange........... | A | 27 | 1–5 | .279 |
| Rubidoux sour orange......... | A | 33 | 6–10 | .275 |
| Sampson tangelo.............. | A | 31 | 6–10 | .273 |
| Lemon shaddock.............. | A | 33 | 11–13 | .273 |
| Sampson tangelo.............. | A | 30 | 6–10 | .272 |
| African sour orange........... | A | 30 | 11–15 | .271 |
| Brazilian sour orange.......... | A | 29 | 1–5 | .271 |
| Rubidoux sour orange......... | A | 28 | 1–5 | .268 |
| Siamese shaddock............ | A | 32 | 1–5 | .266 |
| Brazilian sour orange.......... | A | 29 | 11–15 | .261 |
| C.E.S. 362 sweet orange....... | A | 29 | 6–10 | .258 |
| Trifoliate orange............. | C | 20 | 1–5 | .239 |
| Trifoliate orange............. | A | 27 | 11–15 | .238 |
| Trifoliate orange............. | A | 21 | 1–5 | .234 |
| Trifoliate orange............. | A | 22 | 6–10 | .231 |
| Cleopatra mandarin........... | A | 32 | 11–15 | .230 |
| Trifoliate orange............. | B | 18 | 11–15 | .223 |
| Cleopatra mandarin........... | A | 31 | 11–15 | .222 |

These results for soluble and total calcium, magnesium, and potassium show marked effects of the rootstock variety on the cation accumulation in the leaves of the scion. The type of accumulation in certain respects follows the same trend as that which the seedling root imposes upon the leaves of the seedling tree. Other accumulations, including those of the anions in leaves, may now be examined to determine whether there is any rootstock influence.

*Total nitrogen including nitrates*

The data for total nitrogen obtained for Valencia orange leaves of trees on various rootstocks are arranged in descending order in table 7. Koethen sweet orange occupies the two highest positions in the list, and it is of interest that the plots were 7 rows apart. Rough lemon, grapefruit, sweet orange, tangelo, and lemon shaddock rootstock varieties are in the upper half of the list, whereas Siamese shaddock, trifoliate and sour oranges, citrange and Cleopatra mandarin rootstocks are, for the most part, in the lower part.

The Valencia orange trees on trifoliate orange rootstock were notably tardy in their flowering as compared with similar scions on other rootstocks. On trifoliate orange rootstock more vigor was evident in the vegetative phase of

### TABLE 9

*Total phosphorus in mature Valencia orange leaves of trees grown on various rootstocks in C.E.S. Field S 1*

| ROOTSTOCK VARIETY | ROW | TOTAL PHOS- PHORUS IN DRY MATTER | ROOTSTOCK VARIETY | ROW | TOTAL PHOS- PHORUS IN DRY MATTER |
|---|---|---|---|---|---|
| | | *per cent* | | | *per cent* |
| Koethen sweet orange....... | 35 | .156 | C.E.S. 343 grapefruit...... | 36 | .118 |
| Trifoliate orange........... | 18 | .154 | Rough lemon.............. | 30 | .117 |
| Trifoliate orange........... | 27 | .143 | Brazilian sour orange...... | 29 | .117 |
| Trifoliate orange........... | 20 | .136 | Rubidoux sour orange..... | 28 | .116 |
| Trifoliate orange........... | 22 | .131 | Siamese shaddock.......... | 32 | .116 |
| C.E.S. 343 grapefruit........ | 33 | .129 | Duncan grapefruit......... | 34 | .115 |
| Koethen sweet orange....... | 28 | .128 | Trifoliate orange.......... | 21 | .114 |
| Savage citrange............. | 23 | .128 | Rough lemon.............. | 32 | .114 |
| Duncan grapefruit.......... | 31 | .127 | C.E.S. 362 sweet orange.... | 29 | .113 |
| Sampson tangelo............ | 31 | .125 | Cleopatra mandarin........ | 32 | .113 |
| C.E.S. 362 sweet orange..... | 36 | .125 | Siamese shaddock.......... | 35 | .113 |
| Sampson tangelo............ | 30 | .124 | Savage citrange........... | 22 | .112 |
| Brazilian sour orange........ | 29 | .123 | African sour orange........ | 30 | .108 |
| Cleopatra mandarin......... | 31 | .122 | Rubidoux sour orange..... | 33 | .104 |
| African sour orange......... | 27 | .121 | Lemon shaddock........... | 33 | .103 |

growth of the Valencia orange scions than when these same scions were grown on other rootstocks. The vigor in growth shown by the scions on trifoliate orange rootstock may account in part for the variations in the total nitrogen found in the leaves of the scion (table 7). In such cases soil composition, in respect to nitrogen or some factor related to the deciduous nature of the rootstock as a seedling, may account for some differences in the composition of the leaves. The African sour orange plot values varied widely, and possibly soil variation in addition to the varietal nature of the rootstock may be an important factor, for it was noted that the potassium and calcium values for this same rootstock tended also to vary more widely than the other types of sour orange rootstock. There is no reason for assuming that all sour orange rootstocks of necessity show similar behavior.

*Total sulfur*

The values for the total sulfur content of Valencia orange leaves from trees on various rootstocks are arranged in descending order in table 8. The lowest values are roughly equal to 70 per cent of the highest value. Rough lemon, grapefruit, citrange, and most of the sweet orange rootstocks are in the upper part of the list, whereas sour and trifoliate oranges and Cleopatra mandarin are in the lower part. Although considerable research has been done on the relation of sulfate and boron to nitrogen in citrus leaves, no reference has been made to the nature of the rootstock variety.

TABLE 10

*Total phosphorus in mature citrus leaves of several scion varieties grown on sweet and sour orange rootstocks*

| DATE OF COLLECTION | SCION VARIETY | ROOTSTOCK VARIETY | C.E.S. PATH. PLOT | | TOTAL PHOS-PHORUS IN DRY MATTER |
|---|---|---|---|---|---|
| | | | Row | Trees | |
| *1930* | | | | | *per cent* |
| October 3 | Navel orange | { Sweet orange | 13 | 1,2 | .194 |
| | | Sour orange | 6 | 1,2,4 | .175 |
| October 3 | Eureka lemon | { Sweet orange | 30 | 6 | .134 |
| | | Sour orange | 30 | 2 | .124 |
| October 3 | Marsh grapefruit | { Sweet orange | 18 | 2 | .161 |
| | | Sour orange | 18 | 6 | .137 |
| December 11 | Navel orange | { Sweet orange | 13 | 3,4 | .201 |
| | | Sour orange | 6 | 5,6,7 | .203 |
| December 11 | Eureka lemon | { Sweet orange | 30 | 7 | .110 |
| | | Sour orange | 30 | 3 | .105 |
| December 11 | Marsh grapefruit | { Sweet orange | 18 | 3 | .116 |
| | | Sour orange | 18 | 7 | .107 |

*Total phosphorus*

The total phosphorus values given in table 9 were determined in the dry matter of Valencia orange leaves collected from trees on various rootstocks. The difference between the highest and lowest values was approximately 35 per cent of the highest value obtained. Sweet and trifoliate orange rootstocks generally rank relatively high in table 9, whereas sour orange, rough lemon, and lemon shaddock rootstocks generally rank relatively low.

Table 10 gives the phosphorus values for orange, lemon, and grapefruit leaves of trees on sweet and sour orange rootstocks respectively. In most cases the dry matter in the leaves of the scions on sweet as compared with sour orange rootstocks contained higher percentages of phosphorus.

Reference again to table 4 shows that the leaves of trifoliate and sweet orange seedling trees contained more phosphorus than those of sour orange seedling trees.

A. R. C. HAAS

### RESULTS WITH CITRUS ROOTLETS

The study of the nutrition of rootstocks through the foregoing determinations on the leaves was supplemented next by chemical analyses of the rootlets of four common rootstocks in the Valencia orange orchard. The results are shown in table 11.

The concentration of total sugars is very low in the rootlets of the rootstocks tested. The total (as reducing) sugars in the rootlets of Koethen sweet orange rootstock are somewhat lower than in those of the Standard sour orange root-

### TABLE 11

*Chemical composition of dry matter of rootlets\* of rootstocks of trees with Valencia orange scions*

| ROOTSTOCK VARIETY | Row | Trees | REDUCING SUGAR IN DRY MATTER | TOTAL AS REDUCING SUGAR IN DRY MATTER | TOTAL SULFUR IN DRY MATTER | TOTAL N INCLUDING NITRATES IN DRY MATTER | TOTAL PHOSPHORUS IN DRY MATTER | ACID-INSOLUBLE RESIDUE IN DRY MATTER | CALCIUM IN DRY MATTER Water-soluble | Water-insoluble | Total | MAGNESIUM IN DRY MATTER Water-soluble | Water-insoluble | Total | POTASSIUM IN DRY MATTER Water-soluble | Water-insoluble | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent | per cent |
| Koethen sweet orange....... | 39 | 6–10 | 0.94 | 1.91 | .35 | 1.690 | .108 | 9.81 | .20 | 0.77 | 0.97 | .13 | .16 | .29 | 1.07 | .12 | 1.19 |
| Standard sour orange....... | 25 | 6–10 | 0.90 | 2.34 | .16 | 1.376 | .071 | 2.82 | .12 | 1.90 | 2.02 | .06 | .11 | .17 | 0.50 | .15 | 0.65 |
| Duncan grapefruit......... | 31 | 6–10 | 1.06 | 2.26 | .33 | 1.856 | .137 | 3.36 | .21 | 1.43 | 1.64 | .14 | .08 | .22 | 0.98 | .11 | 1.09 |
| Rough lemon... | 30 | 6–10 | 0.81 | 2.74 | .20 | 1.504 | .093 | 2.45 | .13 | 1.25 | 1.38 | .06 | .13 | .19 | 0.70 | .10 | 0.80 |
| *Acid-insoluble, residue-free dry matter basis* | | | | | | | | | | | | | | | | | |
| Koethen sweet orange....... | 39 | 6–10 | 1.04 | 2.12 | .39 | 1.876 | .119 | | .22 | 0.85 | 1.07 | .14 | .18 | .32 | 1.19 | .13 | 1.32 |
| Standard sour orange....... | 25 | 6–10 | 0.93 | 2.41 | .17 | 1.417 | .073 | | .12 | 1.95 | 2.07 | .06 | .11 | .17 | 0.51 | .15 | 0.66 |
| Duncan grapefruit......... | 31 | 6–10 | 1.10 | 2.34 | .34 | 1.921 | .141 | | .22 | 1.48 | 1.70 | .14 | .08 | .22 | 1.01 | .11 | 1.12 |
| Rough lemon... | 30 | 6–10 | 0.83 | 2.81 | .21 | 1.543 | .095 | | .13 | 1.28 | 1.41 | .06 | .13 | .19 | 0.72 | .10 | 0.82 |

\* Rootlets collected October 18, 1944.

stock. These values for the rootlets are much lower than those found for Valencia orange leaves of the scions on these rootstocks. Factors in addition to the rootstock, and as yet not understood, probably are responsible for the percentage of total (as reducing) sugars found in the dry matter of the leaves of the Valencia orange scions. The percentage values obtained for the leaves of duplicate plots showed close agreement, as for example: Brazilian sour orange (row 29, trees 11–15) 4.54 and (row 29, trees 1–5) 4.46; Rubidoux sour orange (row 28, trees 1–5) 3.63 and (row 33, trees 6–10) 3.58; C.E.S. 362 sweet orange (row 29, trees 6–10) 4.22, and (row 36, trees 1–5) 4.14; Koethen sweet orange

(row 28, trees 6–10) 3.50 and (row 35, trees 1–5) 3.42; and rough lemon (row 30, trees 1–5) 4.46 and (row 32, trees 6–10) 4.34. It was noted, however, that the values for the trifoliate orange plots were nonuniform, and this may be due to factors peculiarly related to this rootstock (such as being deciduous when unbudded). The values for the African sour orange plots also were nonuniform in the same relative order (row 27, trees 1–5) 4.99 and (row 30, trees 11–15) 4.06 as were the discordant results of African sour orange plots for total nitrogen in the Valencia orange leaves on these trees (table 7). Among the thirty plots the scion (Valencia orange) leaves of which were tested for total (as reducing) sugars, the Koethen sweet orange plots were third and fifth lowest respectively. Although there was fair agreement for the plots of a given rootstock (trifoliate orange and African sour orange, exceptions already noted), there were differences between the values for the various sweet orange and sour orange rootstocks. This may mean that the Valencia orange leaves of trees on certain rootstocks retain or store sugars longer than the Valencia orange leaves of trees on other rootstocks, or it may mean that the current production of sugars is not uniform in Valencia orange leaves collected at the same time from trees on different rootstocks. Further investigation in this regard is necessary.

The content of total sulfur is least in the sour orange and rough lemon rootlets. It will be recalled that Valencia orange leaves of trees on sour orange rootstock also contained low total sulfur, though the leaves of trees on rough lemon rootstock contained high total sulfur (table 8). Duncan grapefruit rootlets are high in total sulfur, as are also Valencia orange leaves of trees on Duncan grapefruit rootstock (table 8). Koethen sweet orange rootlets likewise are high in total sulfur, as are Valencia orange leaves of trees on this rootstock (table 8).

The data for the total nitrogen (including nitrates) are given in table 11. Closely agreeing triplicate determinations were used in obtaining the data. The value for sour orange rootlets is the lowest for the rootlets of any of the rootstocks. Reference to table 7 shows that Valencia orange leaves from trees on sour orange rootstock contain relatively low concentrations of total nitrogen. In both tables 11 and 7, the Koethen sweet orange and Duncan grapefruit varieties rank high in total nitrogen content.

Total phosphorus (table 11) is highest in the rootlets of Duncan grapefruit and lowest in those of sour orange. In tables 9 and 10 it was shown that leaves of trees on sour orange rootstock in most cases are lower in total phosphorus than are leaves of trees on sweet orange rootstock. Likewise (table 4) the leaves of seedling sour orange trees contain less total phosphorus than those of seedling sweet orange trees.

Total calcium is highest in sour orange rootlets and lowest in sweet orange rootlets (table 11). Reference to tables 2 and 3 shows that total calcium is higher in orange and grapefruit leaves of trees on sour than on sweet orange rootstock, and in table 4 the leaves of seedling sour orange trees are shown to be higher in total calcium than are the leaves of seedling sweet orange trees.

The sweet orange rootlets (table 11) contained the most magnesium, and

sour orange rootlets the least. This is the converse of the relation shown for grapefruit and orange leaves in table 2.

The rootlets of sweet orange rootstock (table 11) contained almost double the potassium found in the rootlets of sour orange rootstock. This is the same relation as was found in table 2 for potassium in grapefruit and orange leaves from trees on sweet and sour orange rootstocks respectively and was also similar to that shown in table 6 for Valencia orange leaves from trees on these respective rootstocks. Reference to table 4 shows that the leaves of seedling sweet orange trees are also much higher in potassium content than are leaves of seedling sour orange trees. Thus the influence of the rootstock on the composition of citrus leaves is best studied when the leaves of seedling trees and the rootlets of budded trees are also given supplementary consideration.

## SUMMARY AND CONCLUSIONS

The rootstock of citrus trees affects the accumulation of nutrient elements in the leaves and rootlets. The sampling of leaves from orchard trees for chemical analysis may have greater significance when the rootstock variety is taken into consideration.

More calcium and magnesium and less potassium were found in grapefruit and navel and Valencia orange leaves of trees on sour than on sweet orange rootstocks. Valencia orange leaves of trees on shaddock, trifoliate orange, rough lemon, and Cleopatra mandarin are relatively high in magnesium content, whereas those of trees on grapefruit rootstocks are relatively low.

The highest total nitrogen content in Valencia orange leaves was found on trees on Koethen sweet orange rootstock.

Leaves of Valencia orange trees on rough lemon, grapefruit, citrange, and most sweet orange rootstocks contain relatively high amounts of total sulfur in comparison with that in leaves of trees on sour or trifoliate orange and Cleopatra mandarin rootstocks.

Total phosphorus was found to be relatively high in Valencia orange leaves when the trees were on sweet or trifoliate orange rootstocks and was generally low when the trees were on sour orange, rough lemon, and lemon shaddock rootstocks. Leaves of other orange, lemon, and grapefruit trees in most cases contained more total phosphorus when on sweet orange than on sour orange rootstocks.

Leaves of large seedling sour orange trees contained more calcium and magnesium, less total phosphorus, and about half as much potassium as did leaves of large seedling sweet orange trees.

Data from rootstocks with Valencia orange scions show that the rootlets of sour orange are high in calcium and low in potassium, total nitrogen, sulfur, and phosphorus when compared with the rootlets of Koethen sweet orange rootstock.

It is concluded that for orange trees the relative order or type of absorption of nutrient elements which seedling trees impose upon their own leaves resembles in certain respects the order which these seedlings, as rootstocks, impress upon the leaves of the scion variety.

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# SOIL-PLANT RELATIONS: II. BALANCED FERTILIZER USE THROUGH SOIL TESTS FOR POTASSIUM AND PHOSPHORU [1]

ROGER H. BRAY[2]

*Illinois Agricultural Experiment Station*

The ultimate objective in soil fertility studies has been to gain sufficient knowledge of soil-plant relations to enable each farmer to put into practice a balanced fertility program. The most promising recent attack on this problem has been the development and refinement of chemical soil tests and their correlation with crop needs and response to fertilizers. Recently it was shown that the soil tests for potassium and phosphorus developed by the writer (1, 2) accurately measure the available forms of these nutrients in soils and indicate the percentage increase in yield which can be expected when adequate amounts of these nutrients are used (3, 4, 5, 6).

Measuring the available forms and calculating their sufficiencies in terms of the percentage yield is the first step toward determining the amount of a given form of a nutrient needed on a specific soil, that is, the fertilizer requirement. The correlation between the amounts of the available forms and the percentage yield (where the yield on the adequately treated plots is taken as 100 per cent) gives a curve similar to the Mitscherlich growth curve. For this reason it has been assumed that fertilizer response will also follow the Mitscherlich growth curve. This assumption appears reasonable in view of the data contained in the well-known and extensive literature on the subject. It is the purpose of this paper to correlate the soil test values for phosphorus and potash with fertilizer needs through the application of the Mitscherlich equation.

## APPLYING MITSCHERLICH EQUATION TO CALCULATION OF FERTILIZER REQUIREMENTS

The original Mitscherlich equation was used mainly for analyzing the results of fertilizer experiments where responses to several increments of a given nutrient had been measured, one of the objectives being the calculation of the effectiveness of the nutrient already present in the soil in terms of the fertilizer added. In the studies by the writer referred to above, these forms of phosphorus and potassium were measured directly by soil tests, making it possible to employ a modified Mitscherlich equation which did not contain the term $x$ (the fertilizer added).

In this work the values of $c_1$ and $b_1$ for phosphorus and potassium in the following modified Mitscherlich equation (6) were determined for various crops and expressed mathematically:

$$\log (A - y) = \log A - c_1 b_1 \qquad (1)$$

where $A$ = yield when nutrient is adequate, $y$ = yield obtained, $c_1$ = proportionality constant, and $b_1$ = amount of nutrient in the soil as measured by the soil test.

Here $A$ is not a "theoretical" maximum yield obtained where none of the nutrients are deficient. Rather, it is the yield obtained in any case where the one nutrient under consideration is adequate.

### TABLE 1

*Relation between yield without added potash\* and soil test values for available potassium*

| AVAILABLE POTASSIUM $(b_1)$ | YIELD WITHOUT ADDED POTASH | | |
|---|---|---|---|
| | Corn or clovers $(c_1 = 0.0065)$ | Soybeans $(c_1 = 0.0077)$ | Wheat or oats $(c_1 = 0.012$ |
| *lbs./A.* | *per cent* | *per cent* | *per cent* |
| 40 | 45 | 51 | 66 |
| 60 | 60 | 65 | 80 |
| 80 | 70 | 76 | 90 |
| 100 | 78 | 83 | 94 |
| 130 | 85 | 90 | 97 |
| 150 | 90 | 93 | 98 |
| 200 | 95 | 97 | |
| 300 | 98 | | |

\* Where yield with adequate potash is 100 per cent.
Soil requirements for approximately a 98 per cent yield:
    Corn or clovers = 300 pounds per acre of exchangeable K
    Soybeans = 250 pounds per acre of exchangeable K
    Wheat or oats = 150 pounds per acre of exchangeable K
Amount for approximately a 50 per cent yield:
    Corn or clovers = 46 pounds per acre of exchangeable K
    Soybeans = 39 pounds per acre of exchangeable K
    Wheat or oats = 24 pounds per acre of exchangeable K

The value of $c_1$ was found to be essentially a constant for a given crop on different soils varying rather widely in their productivity. But, contrary to Mitscherlich's original findings, a different $c_1$ value was found for each crop.

This means that the level of the nutrient in the soil needed to produce a maximum yield differs for each crop. Each crop, therefore, has its own level of each nutrient for maximum yields. In this paper a 98 per cent yield is used as a practical maximum because the theoretical requirement for the last 2 per cent is large and indefinite. The level of the nutrient in the soil needed to achieve this maximum yield for a given crop is called the "soil requirement" of that crop. For example, table 1 gives the soil requirement of corn for potassium as 300 pounds per acre of exchangeable potassium. This is a constant for corn, within limits, and does not change appreciably for corn-belt conditions. Any value

of $b_1$ lower than 300 pounds, therefore, will produce a lower yield, which will be approximately a constant percentage of the maximum yield.

This is illustrated by the following example: The value of $c_1$ for exchangeable potassium for corn in corn-belt soils is approximately 0.0065. To obtain a 98 per cent yield, $b_1$ must be 300 pounds per acre (150 p.p.m.) of K and log $(100 - 98) = \log 100 - (0.0065 \times 300)$. On the other hand, when $b_1$ is 50 pounds per acre, log $(100 - y) = \log 100 - (0.0065 \times 50)$, and solving, $y = 53$ per cent.

### TABLE 2

*Relation between yield without added phosphate\* and soil test values for available phosphorus*

| AVAILABLE PHOSPHORUS | | YIELDS WITHOUT ADDED PHOSPHATE | | |
|---|---|---|---|---|
| Test Reading | $(b_1)$ | Wheat or clovers ($c_1 = 0.009$) | Corn ($c_1 = 0.015$) | Soybeans† or oats ($c_1 = 0.017$) |
| | *lbs./A‡* | *per cent* | *per cent* | *per cent* |
| Low− | 36 | 53 | 71 | 76 |
| Low | 50 | 65 | 82 | 86 |
| Low+ | 60 | 71 | 87 | 90 |
| Slight− | 70 | 75 | 91 | 93 |
| Slight | 80 | 81 | 94 | 95 |
| Slight+ | 90 | 84 | 96 | 97 |
| Medium− | 110 | 90 | 97 | 98 |
| Medium | 125 | 93 | 98 | |
| Medium+ | 170 | 97 | | |
| High− | 190 | 98 | | |

\* Where yield with adequate phosphate is 100 per cent.

† Estimated percentage yield values for soybeans; probably too low.

‡ Corresponding value at 1–50 soil-solution ratio.

Soil requirements for approximately a 98 per cent yield:

| | Test value | P in lbs./A. |
|---|---|---|
| Wheat or clovers | H− | (190) |
| Corn | M | (125) |
| Soybeans or oats | M− | (110) |

Amount for approximately a 50 per cent yield:

| | P in lbs./A. |
|---|---|
| Wheat or clovers | 33 |
| Corn | 20 |
| Oats or soybeans | 18 |

A soil containing 50 pounds of potassium per acre can be changed to a 98 per cent soil by addition of fertilizer. The complete equation (4) then becomes

$$\log (100 - 98) = \log 100 - (0.0065 \times 50 + cx)$$

where $x =$ the amount of $K_2O$ (added as KCl) needed for a 98 per cent yield, and $c =$ proportionality constant for $x$. Stated in general terms this becomes

$$\log (A - y) = \log A - (c_1 b_1 + cx) \tag{2}$$

Tables 1 and 2 give all the data needed to solve this equation except the value of $c$. Once $c$ is determined for a given crop and a given nutrient, the fertilizer

requirement, $x$, can be calculated. It will then be possible to test a soil (*i.e.*, obtain its $b_1$ value) and from this test calculate directly its fertilizer requirement.

It is the purpose of this paper to apply the above findings and show how the approximate values of $c$ and $x$ for potash and phosphate for various crops can be calculated and used in a balanced fertility program.

### CALCULATING THE FERTILIZER REQUIREMENTS OF CORN-BELT SOILS

Corn-belt soils vary over a wide range in their available nutrients and hence in their productiveness. This means that the fertilizer requirements differ correspondingly. To calculate the fertilizer requirements for a given crop for each soil test value, one must know the effectiveness of the added fertilizer (expressed in the value of $c$), as already explained. It is impossible to determine accurately the specific effectiveness of the fertilizer for each crop by continuous field studies when crops are used in rotation, but it is possible to determine a satisfactory requirement for the rotation as a whole, over a limited period of years. This rotation requirements can then be apportioned to the individual crops in the rotation by assuming that the differences between the amounts actually present ($b_1$) and the soil requirements (at 98 per cent) are measures of the relative fertilizer requirements. Once the rotation requirement is apportioned, equation (2) can be solved for $c$, where $A = 100$ per cent yield, $y = 98$ per cent yield, $c_1 =$ proportionality constant of $b_1$, $b_1 =$ soil test value, $x =$ fertilizer requirement, and $c =$ proportionality constant of $x$.

### Potash requirements

In equation (2) every value is known (see table 1) except $c$ and $x$. The value of $x$ for two cases has been estimated as follows:

On two of the Illinois experiment fields most deficient in potassium, the soils contain about 50 pounds of exchangeable potassium per acre ($b_1$), and 400 pounds of 50 per cent muriate of potash is applied for the 4-year rotation where corn, oats, clover, and wheat are grown. On these fields the yields are approximately doubled by the use of this amount (400 pounds) of muriate, and additional potash gives only slight increases on some crops. This indicates that 400 pounds is approximately the rotation requirement. This is broken down into individual fertilizer requirements for each crop by assuming that the difference between $b_1$ at 98 per cent yield (the soil requirement for a 98 per cent yield) and $b_1$ found on these two fields (the soil test value of 50 pounds per acre) is a measure of the relative need of each crop. Table 1 gives the values of $b_1$ for potassium at 98 per cent. These are 300 each for corn and clovers and 150 each for wheat and oats.

The differences between these values and the 50 pounds test value are 250 each for corn and legumes and 100 each for wheat and oats. (This is the deficiency in exchangeable K for maximum yields and is, therefore, closely related to the fertilizer requirement.) The sum is 700 and the proportion of each is 0.36, 0.36, 0.14, and 0.14 for corn, clover, wheat, and oats respectively. This gives $400 \times 0.36 = 144$ pounds of muriate of potash each for corn and clover and 56

pounds each for wheat and oats. Substituting these values for $x$ in equation (2) gives the values of $c$ for each crop. Once $c$ is known, values of $x$ for different values of $b_1$ can be calculated. Table 3 gives the values of $c$ for the different crops and the calculated muriate of potash requirements for different $b_1$ (soil test) values.

### Phosphate requirements

Table 2 gives all the data necessary to calculate the phosphate requirements once a value of $x$ for one $b_1$ value is known. Again, experiment field work has

#### TABLE 3

*Approximate muriate of potash requirements (0-0-50) of individual crops for each soil test value*

| AVAILABLE POTASSIUM BY TEST ($b_1$) | POTASH REQUIREMENTS FOR DIFFERENT CROPS IN TERMS OF MURIATE OF POTASH (50 per cent $K_2O$) | | |
|---|---|---|---|
| | Corn or clovers ($c = 0.0094$) | Soybeans ($c = 0.015$) | Wheat or oats ($c = 0.020$) |
| lbs./A. | lbs./A. | lbs./A. | lbs./A. |
| 40 | 152 | 94 | 62 |
| 60 | 136 | 84 | 50 |
| 80 | 124 | 72 | 36 |
| 100 | 110 | 62 | 24 |
| 130 | 92 | 46 | |
| 150 | 74 | 36 | |
| 200 | 40 | | |

#### TABLE 4

*Approximate superphosphate requirements (0-20-0) of individual crops for each soil test value*

| AVAILABLE PHOSPHORUS (SOIL TEST VALUE) | SUPERPHOSPHATE REQUIREMENTS FOR DIFFERENT CROPS IN TERMS OF 20 PER CENT SUPERPHOSPHATE | | |
|---|---|---|---|
| | Wheat or clovers ($c = 0.0082$) | Corn ($c = 0.013$) | Soybeans or oats ($c = 0.015$) |
| | lbs./A. | lbs./A. | lbs./A. |
| Low− | 167 | 91 | 75 |
| Low | 154 | 75 | 58 |
| Slight− | 132 | 50 | 36 |
| Slight | 120 | 36 | 27 |
| Medium− | 86 | 13 | |
| Medium | 68 | | |
| Medium+ | 22 | | |

indicated that about 500 pounds of 20 per cent superphosphate per rotation (1,500 of rock phosphate as a general application) has been approximately adequate for the lowest testing soils (low−). The crop requirements for the test readings were then calculated as described above for potassium. These are given in table 4. Numerical values for $b_1$ in place of the test readings of low−, low, low+, etc. were used in these calculations. They were obtained by a quantitative laboratory procedure, using the soil test extracting solution but at

1:50 soil-solution ratio.  The soil test used was the writer's acid-fluoride method for the adsorbed and acid-soluble forms of phosphorus (2).

## A BALANCED FERTILITY PROGRAM FOR PHOSPHATE AND POTASH FOR CORN-BELT SOILS

A balanced fertility program for phosphate and potash is one in which these two nutrients are applied in the amounts needed to complement the soil supplies. The rapid soil tests form the backbone of this program.  They determine in a quantitative way the amounts of the available nutrients already present in each soil.  Through correlations of the tests with experiment field results, the relations between test values and responses (tables 1 and 2) and between test values and the fertilizer requirements (tables 3 and 4) have been established.  In a practical program, balanced fertility is achieved by using the amounts of phosphate and potash indicated by the soil test values.  Because the soil tests are readily and cheaply carried out, balanced fertility can be achieved on each farm field.

This can be illustrated by the following example.  A certain field, where a legume-nitrogen program has been under way for some time, tests "slight" in phosphorus and 80 pounds in exchangeable potassium.  A corn, soybean, wheat, and clover rotation is being followed.  Tables 1 and 2 show the percentage yields which could be obtained on this field with its present soil supplies. For example, potassium limits corn yields to 70 per cent and phosphorus limits them to 94 per cent, the total for both nutrients being their product or 70 per cent $\times$ 94 per cent = 66 per cent, according to Baule's interpretation of Mitscherlich's work, confirmed by the writer (6, 7).  This means that the probable response for the use of both phosphate and potash in adequate amounts is 32 per cent or about half as much again as could be grown without them.  Such calculations are part of the basis for deciding whether or not the treatments may be financially worth while.

Tables 3 and 4 give the fertilizer requirements for each crop, when used in a rotation, and the sum of the fertilizer requirements for each crop is the total amount of each nutrient which should be used during a 4-year rotation.  In this plan, the fertilization of the rotation as a whole is a basic feature, rather than the fertilization of each crop.

The common rotations used in the corn belt have somewhat similar rotation requirements.  It is practical, therefore, to use a single rotation requirement for each test value.  These are given in tables 5 and 6.  In the calculation of these requirements the value of $c_1$ used was the average of the $c_1$ values for corn, soybeans, oats, wheat, and clover.  To continue with the above illustrations, tables 5 and 6 give the rotation requirements for a soil testing 80 pounds in potassium and "slight" in phosphorus.  These are 320 pounds of muriate of potash (50 per cent) and 270 pounds of superphosphate (20 per cent).

Table 7 illustrates one way the rotation requirement can be applied, although several solutions are possible, depending on the type of distributing machinery available.  The rotation requirement is apportioned and applied to each crop

in the rotation according to the best known information about fertilizer use, local soil conditions, the relative crop needs as given in tables 1 and 2, sensitivity or reaction of crops to placement methods, and other factors in crop production such as the relative needs in the seedling stage as compared to the over-all need during the whole growing period.

### Place of other nutrients in a balanced fertility program

Phosphate and potash are only two factors in fertility. Successful production depends on all the factors being sufficiently favorable. The farmer cannot radically change the physical nature of his soil, but he can so farm it as to over-

#### TABLE 5

*Approximate standard rotation requirements (4-year) for potash*

| AVAILABLE POTASSIUM BY TEST | AVERAGE YIELD POSSIBLE WITHOUT POTASH | MURIATE OF POTASH (0-0-50) NEEDED FOR AN AVERAGE 4-YEAR ROTATION |
|---|---|---|
| *lbs./A.* | *per cent* | *lbs./A.* |
| 40 | 53 | 420 |
| 60 | 68 | 370 |
| 80 | 78 | 320 |
| 100 | 85 | 270 |
| 130 | 91 | 200 |
| 150 | 94 | 150 |

#### TABLE 6

*Approximate standard rotation requirements (4-year) for phosphate*

| AVAILABLE PHOSPHORUS (SOIL TEST VALUE) | AVERAGE YIELD POSSIBLE WITHOUT PHOSPHATE | SUPERPHOSPHATE (0-20-0) FOR AN AVERAGE 4-YEAR ROTATION | ROCK PHOSPHATE REQUIREMENT |
|---|---|---|---|
| | *per cent* | *lbs./A.* | *lbs./A.* |
| Low−......................... | 62 | 500 | 1500 |
| Low........................... | 75 | 430 | 1300 |
| Slight−....................... | 85 | 340 | 1000 |
| Slight......................... | 90 | 270 | 800 |
| Medium−..................... | 96 | 120 | |
| Medium....................... | 97 | 70 | |

come partly the effects of adverse physical soil conditions. His methods of farming can improve the water supply to the crop and the physical nature of the surface soil. He can lime, if his soil is acid, and thus overcome any possible deficiencies in calcium and magnesium as well as make the reaction favorable for legume growth. He can maintain a good level of available nitrogen with a good legume program. He can also supply any minor element deficiencies. When he has done these things or made plans for these things, he is in a position to use the balanced fertility program for phosphate and potash described above. In Illinois, the use of phosphate and potash fertilizers of any kind is not generally recommended unless something has been done or is to be done about the nitro-

gen supply, by using animal manures, legumes, synthetic nitrogen, or some other source of supply besides the original humus. The nitrogen program works hand-in-hand with the phosphate-potash program. If the latter nutrients are relatively deficient as well as nitrogen, the two programs should be concomitants; one should not be used alone. Balancing phosphate and potash does not result in a completely balanced fertility program if other factors are out of balance and *vice versa*.

### TABLE 7

*One example of meeting the rotation requirement*

On field 1, farmer A finds his soil testing rather uniformly "slight" in phosphorus and 80 pounds in potassium. He is already using a good legume program. His next four crops will be: 1. a small grain in which mixed clovers will be seeded; 2. mixed clovers; 3. corn; and 4. soybeans.

From rotation requirements, tables 5 and 6, the following data are obtained:

| TEST VALUE | AVERAGE PERCENTAGE YIELD WITHOUT FERTILIZER | REQUIREMENTS | KIND OF FERTILIZER |
|---|---|---|---|
| | | lbs./A. | |
| K = 80 | 78 | 320 | Muriate of potash |
| P = slight | 90 | 270 | Superphosphate |

These can be used in the following manner:

| CROP | METHOD OF APPLICATION | AMOUNT PER ACRE | ANALYSES N–P–K | EQUIVALENT TO | |
|---|---|---|---|---|---|
| | | | | Superphosphate | Muriate of potash |
| | | lbs. | | | |
| 1. Wheat and..... | | | | | |
| 2. Clovers........ | Broadcast | 400 | 0–10–25 | 200 | 200 |
| 3. Corn.......... | Hill-drop | 100 | 0– 9–27 | 45 | 54 |
| 4. Soybeans...... | Broadcast | 100 | 0– 0–50 | | 100 |
| Total........................................................ | | | | 245 | 354 |

### *Definition of a balanced fertility program*

We are now in a position to define a balanced fertility program. A balanced fertility program is one in which the soil supplies of essential nutrient elements are complemented by the proper amounts of fertilizers for the achievement of maximum yield. This balance cannot be achieved with soils deficient in plant nutrients unless the soil supply is first measured by testing before fertilizers are added, since the soil supply varies from soil to soil. The old concept that a certain fertilizer ratio like 2-12-6 or 10-8-6 is a "balanced" fertilizer for a certain crop lost its standing long ago. Such could be the case only for specific conditions, such as a "starter" ratio adapted for the early stage of growth of a certain

crop where the soil supplies are ignored, or on the chance cases in which the soil supply happened to match the complementing fertilizers. Actually the ratio as well as the amount needed changes from soil to soil for the same crop. This concept of balance recognizes the soil requirement of each crop and the soil supplies actually present in each soil. Rotation requirements can possibly be met with existing fertilizer ratios complemented when necessary by single element carriers.

### USE OF SOIL TEST INTERPRETATIONS IN PRACTICE

The use of soil tests to indicate the fact that fertilizer is needed is already a well-established practice in many states. There is no longer any doubt that well-
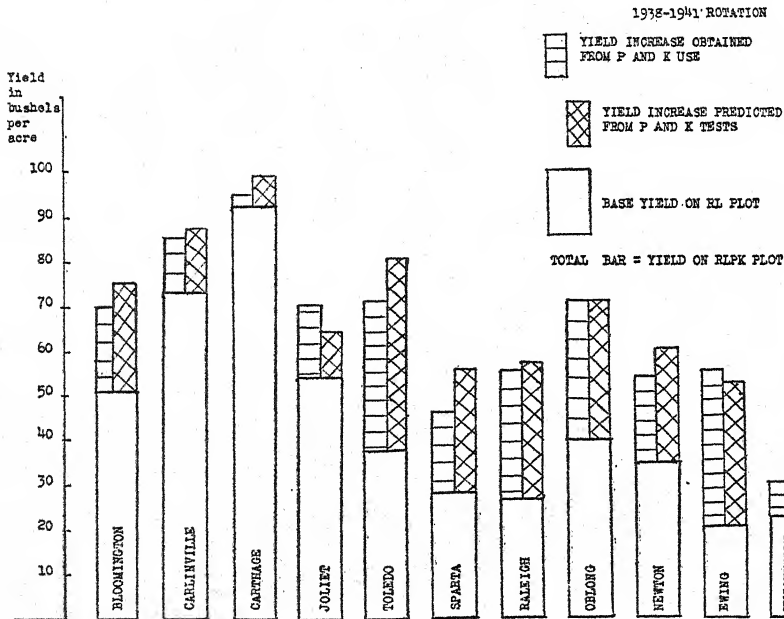


FIG. 1. COMPARISON OF ACTUAL AND CALCULATED INCREASES IN CORN YIELD ON SOIL EXPERIMENT FIELDS

calibrated soil tests are of great value in indicating deficiencies and the degree of these deficiencies (3, 4, 5).

On well-established experiment field plots the writer was able to predict yield increases for the combined use of both potash and phosphate within a standard error of estimate of ±5 per cent. This is illustrated in figure 1.

It is too early as yet to predict how closely the calculated rotation requirements in table 5 and 6 will meet the requirements in practice. They must be considered as tentative values, subject to improvement through further studies, especially field studies, aimed at obtaining the type of data needed for this method of interpretation.

More data are needed involving a series of rates of application of a given nutrient so that the value of $x$ at a specific value of $b_1$ can be determined for more crops. Sufficient is known about the chemistry of exchangeable bases, soil phosphate forms, etc., so that one can now choose a soil representing a specific deficiency and thoroughly study its correction. Field studies aimed at determining whether or not a nutrient is deficient are no longer of as much value as formerly in the case of those nutrients whose available soil forms can be measured by chemical methods. Instead we now need field studies especially designed to give the specific type of information needed for correlating soil test values with the responses and fertilizer requirements of crops.

In Illinois, the soil test interpretation given in tables 5 and 6 are being used as the basis for fertilizer recommendations. Since they involve a knowledge of the nutrient content of the soil and of the response obtained on similar testing soils on the experiment fields, they are far superior to using either test values or experiment field results alone. Furthermore, a sound soil-testing program, where checks are made on the residual build-up of nutrients, will show where excessive amounts are used or where the amounts are insufficient, making it possible to avoid excessive reserves which might be harmful as well as uneconomical.

The program described above is based on complementing the soil supply of available nutrients with fertilizers so as to produce maximum yields. It is obvious that where the fertilizer requirement for phosphorus and potash is less than their removal by crops, the program eventually will be unsound because it will lead to soil depletion. In most soils the available forms of phosphorus and potassium are partly maintained by renewal from unavailable sources. Available phosphorus is renewed by release from decomposition of the original humus. Available potash is renewed by the weathering of potash minerals. As long as the renewal plus the fertilizer added is equivalent to or exceeds the removal, the program remains sound. Sound fertilizer use programs can be based on a good soil-testing program which will show when soil nutrient supplies are being markedly decreased. On some soils this may mean frequent testing. Most corn-belt soils will not require testing oftener than once in 4 to 6 years.

## SUMMARY

The amount of a fertilizer needed to achieve balanced fertility at the maximum yield level depends on the soil supplies and the crop being grown. Supplies of the available forms of a nutrient vary from soil to soil, causing a corresponding variation in the fertilizer requirement.

These soil supplies can be measured directly with the soil tests. This soil test value can be substituted for $b_1$ in the modified Mitscherlich equation

$$\log (A - y) = \log A - (c_1 b_1 + cx)$$

The values of all of these terms except $c$ and $x$ have been previously determined for different crops. The value of $x$ is approximately known for certain cases on the experiment fields for the rotation as a whole. This permits the calculation

of $c$. By using the $c$ values obtained, the approximate fertilizer requirements for each soil test value for phosphorus and potassium have been calculated. These fertilizer requirement values are used in practice in the form of a rotation requirement, which is so applied as to favor the crops with the lowest $c_1$ values (the crops most responsive to the nutrient added). When both phosphate and potash fertilizers are used in these amounts during the rotation they balance the soil forms and make possible a balanced fertility program as far as these two nutrients are concerned. The old idea of a certain ratio of phosphate and potash being needed for a certain crop is not recognized in this plan except insofar as small amounts are used by placement methods for the initial stimulation of the plant.

Where the fertilizer requirement is lower than the amount ultimately removed by crops, a gradual decrease in the available soil supplies will occur unless the rate of supply from the less available soil forms is sufficient to make up for this difference. This is readily checked by a continued soil-testing program which will measure the balance in the soil resulting from crop removals and possible leaching loss, on the one hand, and fertilizer additions and release from less available forms, on the other.

These fertilizer requirements for phosphorus and potassium as determined by the soil tests are not considered recommendations except as they are recommended with a knowledge of the favorableness of the other factors in crop production.

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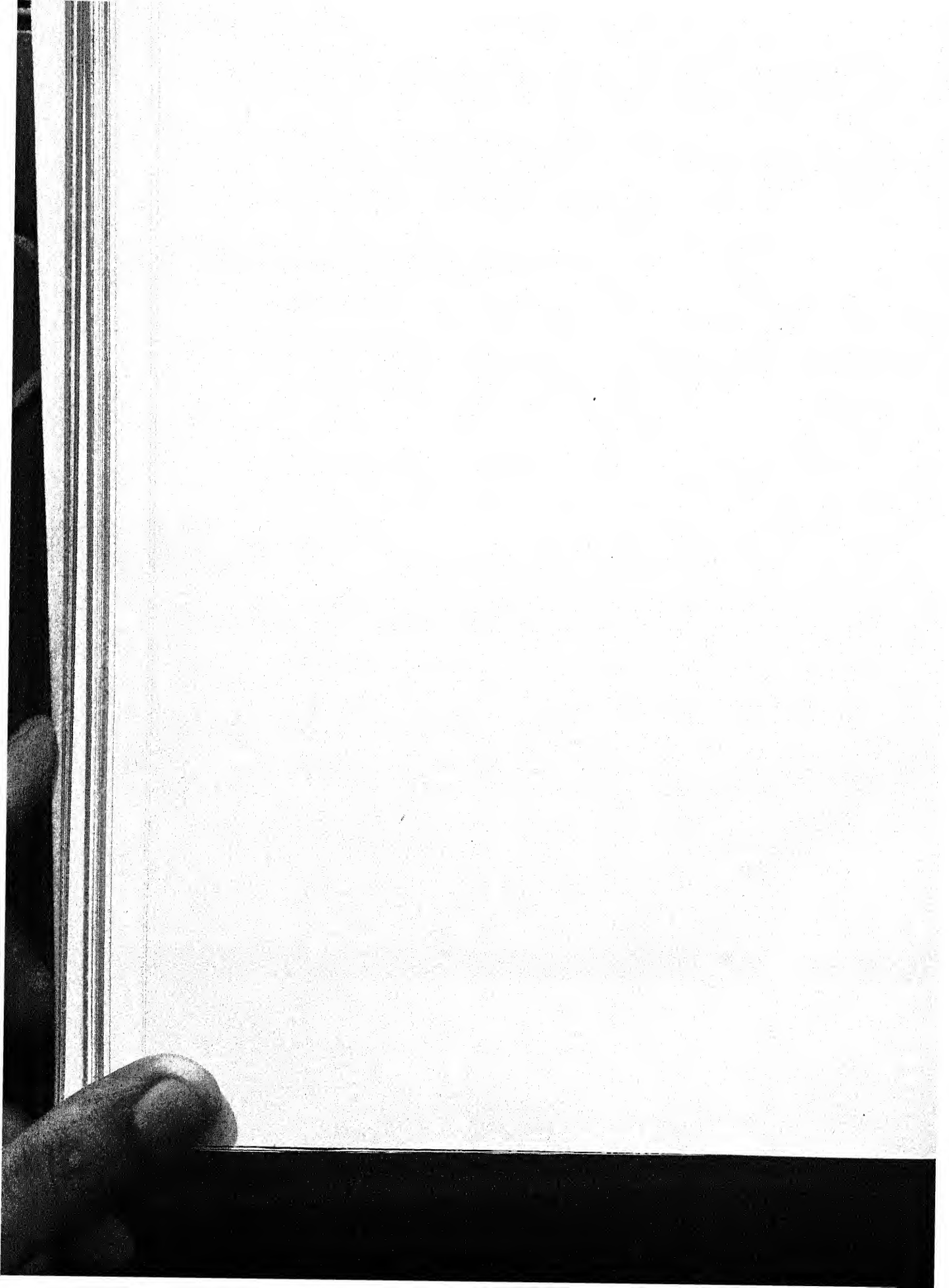
# DYNAMICS OF WIND EROSION: III. THE TRANSPORT CAPACITY OF THE WIND[1]

## W. S. CHEPIL[2]

*Canada Department of Agriculture*

The capacity of air currents for carrying soil material is dependent on the density, velocity, and viscosity of the air. The pressure, or the force, of the wind against a solid object varies directly with density and viscosity of the air and as the square of its velocity.

The viscosity of the air is independent of atmospheric pressure except for very high and very low pressure not common in nature. It varies somewhat with temperature, but on such a scale as may be considered insignificant for all practical purposes.

The density of the air is affected by the temperature, pressure, and humidity. The density of dry air is approximately equal to

$$1.293 \times 10^{-3} \left( \frac{B}{760} \cdot \frac{273}{T} \right) \qquad (1)$$

where $B$ is the barometric pressure in millimeters and $T$ the absolute temperature in °C.

The density of moist air is the sum of the density of water vapor and the dry air. From Dalton's law it follows that if $B'$ is the total barometric pressure of moist air and $p$ is the pressure of the water vapor, then $B' - p$ is the partial pressure of dry air, and the density of the moist air is

$$8.04 \times 10^{-4} \left( \frac{pf}{(760)(100)} \right) \cdot \frac{273}{T} + 1.293 \times 10^{-3} \left( \frac{B' - pf}{(760)(100)} \cdot \frac{273}{T} \right) \qquad (2)$$

where $f$ is the relative humidity expressed in percentage. The pressure of the water vapor varies directly with temperature.

Equation (2) shows that moist air is lighter than dry air at the same temperature and pressure. This may be readily understood if we consider that part of the air is replaced by water vapor, which is lighter than air. Obviously the erosive force of moist wind is lower than that of dry wind.

Inspection of the above relationships will show that a decrease in temperature amounting to 10°C. increases the density of the air, and consequently the wind force, by 2.5 to 4 per cent, depending on the original temperature. It can be observed further that an increase in pressure of 10 mm. of mercury will increase the density of the air by approximately 1.3 per cent. Changes in hu-

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midity likewise have but little effect on the erosive force of wind, and equation (2) indicates that, under the usual conditions, such changes may affect the erosive force to an extent seldom exceeding 3 per cent. The effect of natural variations of air density can therefore hardly be considered significant. A slight change in velocity, however, will cause a considerable change in the force of the wind and presumably also in the quantity of the load which it is able to transport.

The quantity of the load that can be carried by the wind is a matter quite distinct from the size of the soil particle that it can sustain or move along the surface of the ground. The latter question has been covered in detail in a previous publication (5), whereas the object of this paper is to present specific information on the relationship between wind velocity and the rate of removal of the soil.

In this connection, experiments were conducted on fallowed land in the open field and in a portable field tunnel in which simultaneous readings of wind velocity at different heights above ground were taken with a set of six pitot tubes and a specially designed multiple alcohol manometer. At least ten readings were taken and averaged for any one determination.

Wind in the portable field tunnel was fully turbulent, but the magnitude and the velocity of the eddies remained the same for a wide range of wind velocity. Many difficulties were encountered in the open field, where the degree of gustiness varied widely, depending on changes in meteorological conditions. For this reason, it was difficult to obtain much information on the relationship between wind velocity and the rate of soil movement, for a change in wind velocity was sometimes accompanied by a change in gustiness of wind. The gustiness of wind was observed by variations in the rapid consecutive readings of the manometer.

The rate of soil movement in the field tunnel was found by determining the difference in the weight of the soil before and after exposure to the wind and dividing the difference by the duration of exposure. Flow in saltation and surface creep was determined by the Bagnold method (1), and flow in suspension by the difference between the total flow and flow in saltation and surface creep. In the open field, the rate of movement in suspension was not determined, because of the difficulty of accurate measurement, but movement in saltation and surface creep was determined.

In the tunnel the structure of cultivated soils, containing both erosive and nonerosive fractions, changed rapidly with the duration of exposure to the wind, and for this reason it was impossible to establish the relationship between rate of soil movement and wind velocity. The soils were therefore shaken on a 0.83-mm. sieve, and only the fractions passing through the sieve were used in the experiment. These fractions were erosive under all wind velocities used, and under constant velocity their rate of movement remained constant with duration of exposure to the wind. Complete sets of measurements were made during individual wind storms on the leeward sides of fields where soil structure remained constant throughout the course of the investigation. The soil surfaces in the field and in the wind tunnel were very smooth, and surface projections seldom exceeded 0.75 inch in height.

## RESULTS

Typical distributions of wind velocity in a tunnel above an eroding surface composed of erosive fractions are indicated graphically against the logarithm of
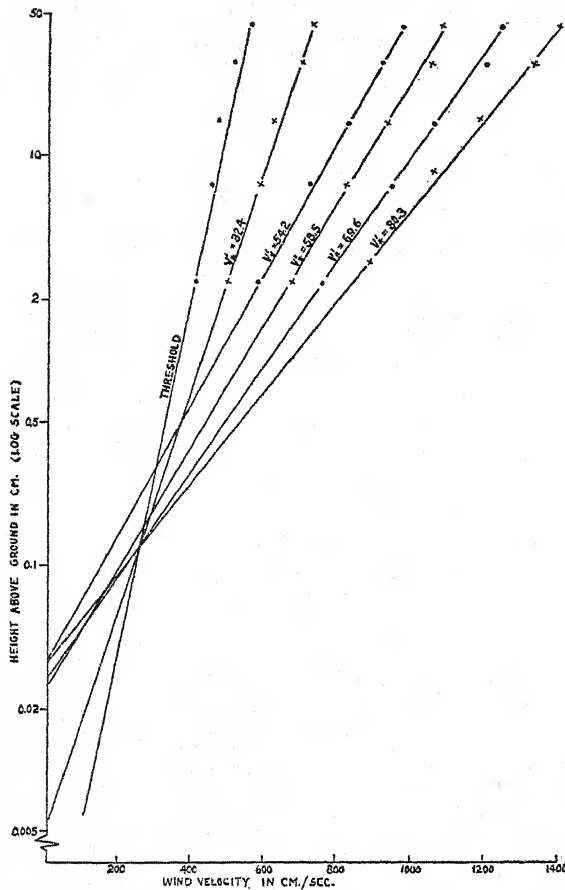


FIG. 1. WIND VELOCITY DISTRIBUTION ABOVE A SMOOTH SURFACE OF HATTON FINE SANDY LOAM IN A WIND TUNNEL

height in figure 1. The velocity $v$ at any height $z$ conforms to Prandtl's logarithmic formula of the form

$$v_z = 5.75 \; V'_* \log \frac{z}{k} \qquad (3)$$

where $V'_*$ is the so-called "drag velocity," which is equal to $\dfrac{v_z}{5.75 \log \frac{z}{k}}$, in which

$k$ is the height at which the projected curves indicate the velocity to be zero. Since the velocity and the log-height have a straight-line relationship, $V'_*$ determines the slope of the velocity distribution curves.

The drag velocities $V'_*$ obtained on different soils were checked against the Bagnold rate of flow formula obtained on desert sand (1), and of the form

$$q = C \frac{\rho}{g} V'^3_*  \qquad (4)$$

where $q$ is the rate of soil flow in grams per centimeter width per second; $\rho$ the density of the air, which, under the conditions of this experiment, was $1.10 \times 10^{-3}$; $g$ the gravity constant 981; and $C$ a constant which seems to vary for different soils and forms of erosion. The smooth curves drawn through the points in figure 2 correspond to the above formula and indicate the degree of agreement
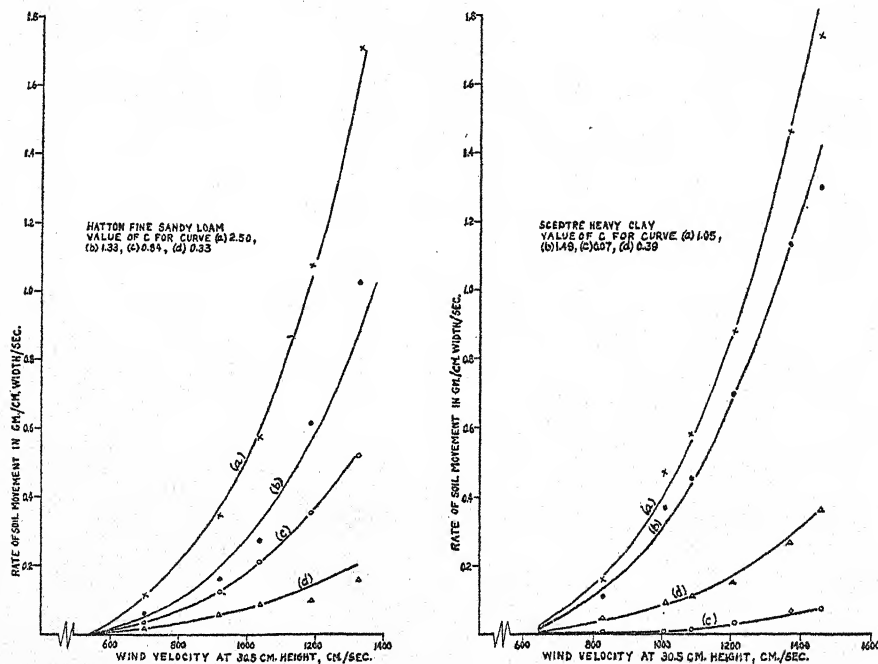


FIG. 2. RELATION OF WIND VELOCITY IN A WIND TUNNEL TO (a) THE TOTAL SOIL FLOW, (b) FLOW IN SALTATION, (c) FLOW IN SUSPENSION, (d) FLOW IN SURFACE CREEP

between the actual and theoretical values. The agreement, on the whole, is good and shows that the above formula applies equally well to flow in suspension as to saltation and surface creep. The data further show that, all other conditions remaining the same, the rate of soil movement varies as the cube of the drag velocity $V'_*$. Similar results were obtained in the wind tunnel on several other widely different soils.

The results in the open field on soils composed of both erosive and nonerosive fractions were in some respects similar to those obtained in the wind tunnel, where the soils were composed only of erosive fractions. The smooth lines drawn through the points in figure 3 correspond to equation (4) and show that the cubic relationship between the drag velocity and the rate of soil movement also holds

good for soil in the open field, but the values of the constant $C$ are somewhat lower than on the same soil type in the wind tunnel. This is apparently due to the removal of nonerosive fractions from all wind tunnel samples, a treatment which undoubtedly increased the erosiveness of the residual fraction.
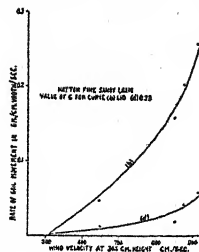


FIG. 3. RELATION OF WIND VELOCITY IN THE OPEN FIELD TO (b) SOIL FLOW IN SALTATION, (d) FLOW IN SURFACE CREEP

## DISCUSSION

The rate of movement of the soil fraction smaller than 0.83 mm. in diameter in the wind tunnel seems to approach the possible maximum flow of the soil from which this fraction is obtained. This rate of movement is equal to that which usually occurs on the leeward sides of large fields of bare soil 80 rods or more in width (2) and denotes the possible maximum load that may be transported by wind of a particular velocity. The values of the constant $C$ in wind tunnel experiments therefore represent the highest possible values for each of the respective soils.

The constant $C$ for the total soil flow varies widely for different soils, the range recorded being 1.0 to 3.1. The value of $C$, as used in equation (4), varies with the degree of erosiveness of the soil, which may be affected by many factors. Bagnold (1) found that the rate of sand movement varies directly with the range of size of the erosive grains and as the square root of their average diameter.

Furthermore, the author (3) asserts that in soils the presence of fine dust smaller than 0.05 mm. in diameter reduces the rate of movement of coarser, more erosive grains. The rate of soil movement has been found to depend also on the size and percentage of the nonerosive fractions present in the soil (3), on the roughness of the soil surface (4), and on the distance within the eroding field (2). All these factors, and perhaps many more, affect the erosiveness of the soil and hence the value of the constant $C$ in the Bagnold equation. Since the subject of the influence of different factors on the relative erosiveness of soils is beyond the scope of the present investigation, it will not be discussed here. The point that should be brought out, however, is that irrespective of the actual erosiveness of the soil, the rate of soil movement varies as the density of the air, the drag velocity, and the degree of gustiness of the wind. Since air density varies but little under natural conditions, the changes in the rate of soil movement, when soil conditions remain the same, must be attributed mainly to the changes in velocity and gustiness of the wind.

## SUMMARY

It has been found that the rate of soil movement in saltation, suspension, and surface creep varies as the cube of the drag velocity of the wind. The rate of soil movement was shown to be only slightly influenced by ordinary changes in air density as affected by changes in air temperature, pressure, and humidity.

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# RETENTION OF PHOSPHATES BY SOILS: III. NATURE OF PHOSPHATE RETENTION OF VIRGIN HAMMOND VERY FINE SANDY LOAM TREATED WITH $Ca(OH)_2$ AND $H_3PO_4$[1]

FRANKLIN L. DAVIS[2]

*Louisiana Agricultural Experiment Station*

Evaluation of all the factors relating to the retention of phosphates by soils has rarely been attempted. Among the factors most commonly studied are the mineral constituents of the soil, the chemical behavior of the colloids, and the hydrogen-ion concentration of the medium. Other factors involved which have received some attention are temperature, length of time of contact, the cations associated with the phosphate, and organic matter. In only a few studies have measurements been made of the possible effect of phosphate fixation upon the cation-exchange capacity of the soil.

In studies previously reported by the author (8, 9) of the effect of additions of ferric and aluminum chlorides upon the retention by virgin Hammond very fine sandy loam of subsequently added phosphates, data were obtained (9) which indicated that increases in cation-exchange capacity resulted from adding monocalcium phosphate. These increases appeared to be related to the amount of monocalcium phosphate added and the amount of calcium present in that form of the calcium ortho-phosphates which existed at the soil reaction at which phosphate fixation occurred. These results did not fully agree with the mechanism of phosphate fixation as postulated by other investigators (1, 15) from valid data obtained with somewhat different soil materials and phosphoric acid.

The data herein reported were obtained from fifty 50-gm. samples of a soil which had been treated previously with systematically varied amounts of $Ca(OH)_2$ and $H_3PO_4$, carbonated with $CO_2$, aspirated for 6 hours with air, and kept in storage in the laboratory. Since the experimental procedure followed and the treatments given these samples were similar to those of the investigators referred to (1, 15), further studies were made on these same samples to determine whether the addition of $H_3PO_4$ to soil increases its cation-exchange capacity and to obtain data concerning possible differences in the manner in which $H_3PO_4$ and monocalcium phosphate react with the same soil.

The literature concerning the possible effect of anion absorption upon the cation exchange capacity of soils has been reviewed elsewhere (9). It should be noted, however, that Mattson and Hester (12) suggested that the absorption of weakly dissociated ions by the soil complex would result in a change in the character and behavior of the soil complex. Toth (16) observed a marked increase in exchange capacity and a reduction in the ultimate pH of phosphate-

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[2] Associate agronomist.

treated colloids.   Ravikovitch (14) found that the liberation, by leaching with
0.05 $N$ HCl, of $PO_4$ adsorbed by H-saturated soils was associated with the
partial destruction of the complex.

### EXPERIMENTAL PROCEDURE AND METHODS

The samples of Hammond very fine sandy loam on which these determina-
tions were made had been treated with $Ca(OH)_2$ and $H_3PO_4$ and equilibrated in
Squibb funnels with $CO_2$ and air in 1938.   The apparatus used has been de-
scribed (8).   The procedure was, briefly, as follows:

Ten 500-ml. Squibb separatory funnels were supported in ordinary funnel racks adapted
for the purpose.   These were located on a laboratory desk where they could be readily
connected by rubber tubing (pressure) through a manifold fitted with gas stopcocks to the
desired source of gas, that is, $CO_2$ or compressed air.   Graduated amounts of distilled $H_2O$
and standardized $Ca(OH)_2$ solution near 0.04 $N$ were measured into each of the funnels.
The volume of water added was adjusted so that the total volume of $H_2O$, $Ca(OH)_2$, and
$H_3PO_4$ solution used was equal to 250 ml. in all samples.   The amount of $Ca(OH)_2$ added
to each sample is given in table 1.   A quantity of air-dried soil equal to 50 gm. of oven-dry
soil was weighed into each funnel.   The funnels were closed with ground glass stoppers
and allowed to stand overnight.

After standing for 16 hours (overnight), the stoppers were removed and the soil samples
were brought into suspension by bubbling air through the soil-$H_2O$-$Ca(OH)_2$ systems.
The desired amount of $H_3PO_4$ was pipetted immediately into each sample, after which $CO_2$
was bubbled through all samples for 15 minutes.   All samples were then aspirated with air
for 6 hours.   Both the $CO_2$ and the air were bubbled through the soil-$H_2O$-$Ca(OH)_2$
systems at a rate sufficient to keep the soil in suspension.

After 6 hours' aspiration with air, the samples were run into 400-ml. beakers, and the
reaction of the suspensions was determined immediately with a Beckman pH electrometer.
The samples were then filtered on a folded filter paper and allowed to drain overnight.
The $H_2O$-soluble phosphorus and calcium in the filtrate were determined.

After being allowed to air-dry thoroughly, the soil samples were removed from the filter
paper, passed through a 1.0-mm. mesh screen, mixed, and placed in screw-cap sample
bottles.   The amounts of phosphorus extracted from the air-dry soil by 0.002 $N$ $H_2SO_4$
(7, 18) after 30-minute shaking and after standing overnight, or 16 hours, were determined.

After 6 years' storage in the bottles, the remainder of the 50-gm. samples was used for
the present investigation, details of which follow.

For the determination of base-exchange capacity, 20-gm. portions of each soil sample
and 100 ml. of distilled $H_2O$ were placed in 250-ml. beakers and stirred; after standing
overnight, the pH values were determined as above.   The samples were then transferred
to 250-ml. Erlenmeyer flasks, each of which contained 11.56 gm. of c.p. $NH_4C_2H_3O_2$, and
made up—by washing the beaker with distilled $H_2O$—to the 150-ml. mark.   The flasks
were shaken intermittently by hand for $3\frac{1}{2}$ hours and then the suspensions were filtered on a
prepared asbestos mat in Gooch crucibles.   All the soil was transferred to the crucible and
leached with an additional 350 ml. of normal ammonium acetate having a pH of 7.07.   A
normal solution of the c.p. ammonium acetate salt used was found by test to have a reac-
tion of pH 7.03.   The soils were washed with 150 ml. of neutral 80 per cent ethanol, and
after moderate drying were transferred to Kjeldahl flasks and the amounts of absorbed
ammonia determined (6, 13).

The phosphorus dissolved in the normal ammonium acetate solution was determined
by the modified Denige's method (17).   Duplicate aliquots were used, and all were diluted
with distilled $H_2O$ to a phosphorus concentration of less than 0.25 p.p.m. and an $NH_4C_2H_3O_2$
concentration of 0.1 to 0.01 $N$.   The remainder of the $NH_4C_2H_3O_2$ leachate was taken to

dryness (6), and the exchangeable calcium determined by the method of Chapman (5) for precipitating calcium oxalate in the presence of Fe, Al, Ti, Mn, Mg, and $PO_4$.

## EXPERIMENTAL RESULTS

The amount of lime which had been added to the respective samples of each series was based on the capacity of the soil to absorb calcium as determined by the method described by Bradfield and Allison (2). The degree of saturation of the soil for each of the quantities of $Ca(OH)_2$ used is shown in table 1.

### TABLE 1

*Treatment and reaction of soil\* immediately after equilibration and after standing in air-dry condition for 6 years*

| Ca(OH)₂ added ...... m.e. Degree of Ca-sorption capacity.... per cent Sample number...... | | 0 0 1 | 2.16 20 2 | 4.32 40 3 | 6.48 60 4 | 8.64 80 5 | 10.8 100 6 | 12.96 120 7 | 15.12 140 8 | 17.28 160 9 | 19.44 180 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatment | Date of determination | pH | pH | pH | pH | pH | pH | pH | pH | pH | pH |
| Ca(OH)₂ only—check | 7/30/38 | 5.38 | 6.1 | 6.8 | 7.3 | 7.75 | 8.0 | 8.15 | 8.28 | 8.35 | 8.4 |
|  | 11/15/44 | 5.48 | 5.9 | 6.15 | 6.42 | 6.7 | 6.9 | 7.15 | 7.38 | 7.7 | 7.75 |
| Ca(OH)₂ + 0.54 mmol. H₃PO₄ | 4/18/38 | 4.9 | 5.9 | 6.48 | 7.0 | 7.4 | 7.7 | 8.0 | 8.2 | 8.28 | 8.35 |
|  | 11/13/44 | 5.42 | 5.9 | 6.2 | 6.4 | 6.7 | 6.88 | 7.17 | 7.25 | 7.5 | 7.75 |
| Ca(OH)₂ + 1.08 mmols. H₃PO₄ | 5/ 9/38 | 4.63 | 5.5 | 6.28 | 6.85 | 7.25 | 7.6 | 7.9 | 8.1 | 8.2 | 8.3 |
|  | 11/10/44 | 5.2 | 5.65 | 6.05 | 6.35 | 6.6 | 6.84 | 7.15 | 7.33 | 7.6 | 7.85 |
| Ca(OH)₂ + 2.16 mmols. H₃PO₄ | 5/21/38 | 3.9 | 4.7 | 5.54 | 6.2 | 6.7 | 7.2 | 7.6 | 7.8 | 7.9 | 8.0 |
|  | 11/ 8/44 | 5.14 | 5.52 | 6.02 | 6.25 | 6.6 | 6.8 | 7.0 | 7.23 | 7.25 | 7.55 |
| Ca(OH)₂ + 4.32 mmols. H₃PO₄ | 7/16/38 | 3.2 | 3.72 | 4.3 | 5.0 | 5.66 | 6.2 | 6.7 | 7.1 | 7.4 | 7.6 |
|  | 11/ 6/44 | 4.85 | 5.15 | 5.45 | 5.91 | 6.2 | 6.45 | 6.64 | 6.85 | 7.0 | 7.04 |

\* All treatments given are for 100 gm. soil. Soil-water ratio = 1:5 in all instances.

Thus, sample number 6 in all series had just sufficient $Ca(OH)_2$ added to saturate the soil with calcium if no other treatments were used. The amounts of $H_3PO_4$ added to the successive series of samples were 0, 0.54, 1.08, 2.16, and 4.32 millimols per 100 gm. of soil.

### Changes in soil reaction

The reactions of the soil-$H_2O$-$Ca(HCO_3)_2$ systems immediately after equilibration with air are given in table 1. The reactions of these soil samples after 6 years' storage in the air-dry condition are also shown in table 1.

The pH values obtained in all series for the samples which had an excess of $Ca(OH)_2$ added indicate that the reactions of the suspensions, after 6 hours' aspiration, had reached or closely approached equilibrium. This is in agreement with the data of Bradfield and Allison (2) that equilibrium with the $CO_2$ of the air in the system clay-$CaCO_3$-$H_2O$ was reached within 4 to 5 hours after car-

bonation with $CO_2$. The pH values obtained after the samples had been kept in the air-dry condition for 6 years show that the reactions changed and indicate that further chemical reaction or rearrangements took place in the soils which had been treated with lime, phosphoric acid, or a combination of the two.

The data in table 1 show that the pH values of all samples in the series to which only $Ca(OH)_2$ was added, with the exception of sample number 1, decreased upon standing in the air-dry condition. Likewise the more acid samples
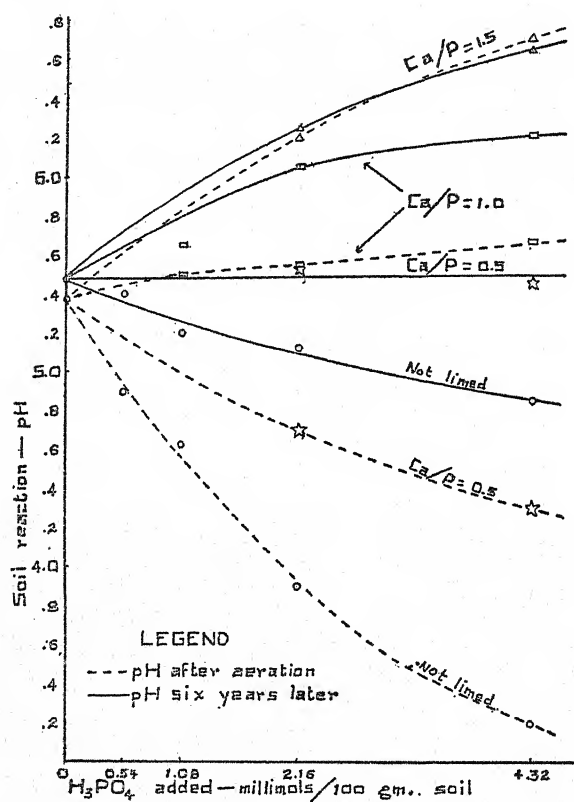


FIG. 1. EFFECT OF TREATMENT WITH $H_3PO_4$ UPON pH VALUES, AND RELATION OF CALCIUM-PHOSPHORUS RATIO OF TREATMENTS TO CHANGES IN REACTION ON STANDING

of the series treated with $H_3PO_4$ became less acid on standing. When these changes in reaction are plotted as functions of the amounts of $H_3PO_4$ and $Ca(OH)_2$ added, it is seen that the increases in pH which occurred on prolonged air-drying of samples number 1 of the series treated with $H_3PO_4$ were larger than the decreases in reaction of comparable samples of the series treated with $Ca(OH)_2$ only. This holds true for the comparison of all levels of $H_3PO_4$ treatment to equivalent $Ca(OH)_2$ treatments. This indicates that the chemical changes which occurred during prolonged air-drying and which resulted from the treatments were larger for $H_3PO_4$ than for $Ca(OH)_2$.

The curves in figure 1 show the effect of treatment with $H_3PO_4$ upon pH values and the relation of the calcium-phosphorus ratio (Ca/P) of the joint treatments with $Ca(OH)_2$ and $H_3PO_4$ to the changes in reaction which occurred on standing.

In the original suspension the treatment with $H_3PO_4$ alone or with $H_3PO_4$ and $Ca(OH)_2$ when Ca/P = 0.5 resulted in more acid reactions. The treatment with $Ca(OH)_2$ and $H_3PO_4$ when Ca/P = 1.0 made the samples slightly less acid, and the samples with treatments having a Ca/P of 1.5 became considerably less acid, but none of them passed pH 7.0. The reactions of the last samples did not change appreciably on air-drying, whereas those having a Ca/P of 1.0 in the treatments became considerably less acid on air-drying. The reactions of the samples treated with $H_3PO_4$ only changed the most. It should be noted that the reactions of the samples for which the Ca/P of the treatments was 0.5 were about the same after prolonged air-drying as the reaction of the untreated soil.

### Changes in cation-exchange capacity

The cation-exchange capacity and the calcium and phosphorus contents of the exchange solutions from all samples of the $H_3PO_4$-treated series are given in table 2.

The data in table 2 show that liming resulted in an increase in cation-exchange capacity in all series regardless of other treatment. The reasons for these increases have been discussed (9). When cation-exchange capacity is plotted as a function of soil reaction, it is seen that the exchange capacity increases to an apparent maximum at the point of saturation of the soil with calcium and then increases at a lesser rate above that point. The curves also show that the point of saturation of the soils with calcium occurs at reactions of pH 7.0–7.1 in the series treated (1) with $Ca(OH)_2$ only, (2) with 0.54 millimol of $H_3PO_4$ and (3) with 1.08 millimols $H_3PO_4$. In the series treated with larger amounts of $H_3PO_4$, that is, 2.16 and 4.32 millimols, the point of saturation of the soil with calcium and the first maximum of increase in cation-exchange capacity occur at lower pH values, that is, at pH 6.6 and 6.8.

The data in tables 1 and 2 show that no significant increase in cation-exchange capacity occurred at reactions below pH 7.0 as a result of adding 0.54 or 1.08 millimols of $H_3PO_4$ per 100 gm. soil. The addition of 2.16 or 4.32 millimols of $H_3PO_4$ produced an increase in the cation-exchange capacity of the soils— the more acid the reaction, the larger the increase.

It appears from the data in table 2 that the amount of $H_3PO_4$ added had but little effect on exchangeable calcium, with the exception of the series receiving 4.32 millimols. In this series the exchangeable calcium in samples having a reaction below pH 7.0 was noticeably reduced by the addition of $H_3PO_4$. In contrast, the amount of phosphorus in the exchange solution increased markedly with increasing amounts of $Ca(OH)_2$ added. It has been shown (9) that the calcium of $CaCO_3$ present in the soil is partly dissolved in salt solutions used for measuring exchange capacity. To all samples numbered above 6, $Ca(OH)_2$

was added in excess of the soil's capacity to absorb calcium. This $Ca(OH)_2$ was theoretically precipitated as the carbonate by carbonation with $CO_2$ and equilibration with air. Partial dissolution of this lime and of any precipitated

### TABLE 2

*Treatment, cation exchange capacity, and exchangeable calcium and phosphorus in exchange solution*

Treatment and results, per 100 gm. soil

| Ca(OH)₂ added.........m.e. Sample number.............. | 0 1 | 2.16 2 | 4.32 3 | 6.48 4 | 8.64 5 | 10.8 6 | 12.96 7 | 15.12 8 | 17.28 9 | 19.44 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| *Cation exchange capacity—m.e.* | | | | | | | | | | |
| $Ca(OH)_2$ only—check. | 7.85 | 8.0 | 8.2 | 8.35 | 8.85 | 9.35 | 9.8 | 9.7 | 9.7 | 9.75 |
| $Ca(OH)_2$ + 0.54 mmol. $H_3PO_4$ | 7.95 | 8.0 | 8.2 | 8.35 | 8.7 | 9.3 | 9.5 | 9.65 | 9.8 | 10.1 |
| $Ca(OH)_2$ + 1.08 mmols. $H_3PO_4$ | 8.0 | 8.0 | 8.15 | 8.35 | 8.6 | 8.9 | 9.3 | 9.4 | 9.6 | 9.9 |
| $Ca(OH)_2$ + 2.16 mmols. $H_3PO_4$ | 8.6 | 8.7 | 8.75 | 9.0 | 9.3 | 9.55 | 9.6 | 9.65 | 9.7 | 10.05 |
| $Ca(OH)_2$ + 4.32 mmols. $H_3PO_4$ | 9.1 | 9.1 | 9.15 | 9.2 | 9.3 | 9.5 | 9.75 | 9.8 | 9.9 | 10.05 |
| *Exchangeable calcium—m.e.* | | | | | | | | | | |
| $Ca(OH)_2$ + 0.54 mmol. $H_3PO_4$ | 0.9 | 2.8 | 4.45 | 6.2 | 7.55 | 9.4 | 10.7 | 11.75 | 13.15 | 13.9 |
| $Ca(OH)_2$ + 1.08 mmols. $H_3PO_4$ | 0.9 | 2.65 | 4.5 | 6.0 | 7.5 | 9.2 | 10.65 | 11.75 | 13.35 | 14.4 |
| $Ca(OH)_2$ + 2.16 mmols. $H_3PO_4$ | 0.8 | 2.45 | 4.25 | 5.95 | 7.7 | 9.55 | 11.05 | 12.6 | 14.2 | 15.2 |
| $Ca(OH)_2$ + 4.32 mmols. $H_3PO_4$ | 0.5 | 1.55 | 3.0 | 4.7 | 6.6 | 8.2 | 9.6 | 11.6 | 13.55 | 15.0 |
| *Phosphorus in exchange solution—mmols. $PO_4$* | | | | | | | | | | |
| $Ca(OH)_2$ + 0.54 mmol. $H_3PO_4$ | 0.04 | 0.05 | 0.06 | 0.08 | 0.09 | 0.10 | 0.12 | 0.13 | 0.13 | 0.13 |
| $Ca(OH)_2$ + 1.08 mmols. $H_3PO_4$ | 0.07 | 0.08 | 0.11 | 0.14 | 0.16 | 0.19 | 0.24 | 0.30 | 0.33 | 0.34 |
| $Ca(OH)_2$ + 2.16 mmols. $H_3PO_4$ | 0.09 | 0.09 | 0.11 | 0.17 | 0.25 | 0.31 | 0.42 | 0.69 | 0.74 | 0.81 |
| $Ca(OH)_2$ + 4.32 mmols. $H_3PO_4$ | 0.20 | 0.19 | 0.20 | 0.27 | 0.32 | 0.55 | 0.79 | 1.18 | 1.39 | 1.57 |

calcium phosphates by the ammonium acetate solution accounts for the fact that the values for exchangeable calcium are higher than the corresponding cation-exchange capacities of all samples having a final pH value of 6.84 and above.

#### DISCUSSION

The changes that occurred in the reaction of the soil samples on being air-dried were due to the changes in the conditions of equilibrium under which the

pH values were determined. When the soil reactions were first measured, the samples were at equilibrium with five times their weight of water and certain soluble materials. When the samples were filtered, the water and $H_2O$-soluble materials were removed, thus destroying the conditions of this equilibrium. As the soil became air-dry new conditions of equilibrium were established, and the soil reaction and solubilities of the soil constituents were thereby affected.

The addition of 0.54 and 1.08 millimols of $H_3PO_4$ per 100 gm. of soil did not result in significant increases in the cation-exchange capacity of the soil similar to those obtained from the addition of 1.08 millimols of P in the form of mono-calcium phosphate (9). A possible explanation of this is that the $H_3PO_4$ was added to the soil-$Ca(OH)_2$-$H_2O$ suspensions after they had stood for 16 hours and before they had been carbonated or brought to equilibrium with the soil. Dunn's data (10), published since these experiments were initiated, showed that stirring continuously for 8 hours or standing with occasional stirring for 4 days is required to establish a pH equilibrium between soils and $Ca(OH)_2$ solution. The data obtained with monocalcium phosphate (9) indicated that phosphates were fixed as the tertiary form, that is, as carbonato-apatite, at reactions of pH 7.7 and above. Breazeale and McGeorge (3) found that plants absorb little or no phosphate at reactions of pH 7.6 and above and showed (11) that the tertiary forms of phosphate exist at these alkaline reactions. Buehrer (4) pointed out that the tertiary phosphate may be a hydroxy-apatite or the carbonato-apatite. Since the $H_3PO_4$ was added before the soil-$Ca(OH)_2$ systems were carbonated or had been brought to a pH equilibrium, it is probable that the hydroxyl ion governed the type of chemical reaction that occurred, that is, the hydroxy-apatite was formed. This compound would not react with the soil as does the carbonato-phosphate to result in an anionic fixation of the phosphate in the tertiary form [see (9)]. Some of the phosphorus supplied by the $H_3PO_4$, however, may have been held in a soil micelle-Ca-phosphate linkage as postulated by other investigators (1, 15).

The addition of $H_3PO_4$ at the higher levels, 2.16 and 4.32 millimols of P per 100 gm. soil, produced increases in the cation-exchange capacity of all samples having an equilibrium reaction of less than pH 6.7. The lower the pH of the sample, the greater the increase in cation-exchange capacity. In the more acid samples of these series the ratios of $Ca(OH)_2$ to $H_3PO_4$ added were lower, and it is possible that the primary and secondary calcium phosphates were formed and these were fixed by the soil as anions producing an increase in the cation-exchange capacity (9). The larger the amount of $Ca(OH)_2$ added, the less was the amount of primary and secondary phosphate formed. Instead the hydroxy-apatite was probably formed and this compound did not react with the soil to produce anionic fixation of phosphate. Further experimental work is necessary to demonstrate definitely that these reactions occur in the presence of soil. But the fact remains that $H_3PO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O$ are different chemical compounds which could scarcely be expected to react similarly with soils.

It could be questioned whether a comparable status of phosphate solubility, nature of phosphate fixation, and equilibrium of the soils would ever be attained

in the same soil when phosphorus is supplied as $H_3PO_4$ or as monocalcium phosphate. Certainly it was not obtained in the time involved in these experiments. Consequently, laboratory data on the fixation of phosphates by soils that have been obtained with different forms of phosphorus and various hydroxides or bases should be interpreted carefully. For the purpose of obtaining a correct understanding of the manner in which phosphates are held by soils under field conditions, laboratory procedures and materials should be as nearly as possible like those existing in actual practice.

## SUMMARY AND CONCLUSIONS

Uniform series of samples of virgin Hammond very fine sandy loam were treated with systematically varied amounts of $Ca(OH)_2$ and $H_3PO_4$, carbonated with $CO_2$, and brought to equilibrium with the $CO_2$ content of the air. Laboratory determinations were made of the reaction, cation-exchange capacity, exchangeable calcium and the phosphates contained in the exchange solution. The data obtained suggest the following conclusions:

When small amounts of phosphorus in the form of phosphoric acid are added to suspensions of a soil in $Ca(OH)_2$ solution, the calcium and hydroxyl ions govern the extent of reversion of the phosphate; that is, the hydroxy-apatite is probably formed and the phosphate is not adsorbed by the soil as anions at pH values above 5.0 except at very low calcium concentrations.

When larger amounts of phosphoric acid are added to soils under the same experimental conditions, some of the phosphorus is reverted to primary or secondary calcium phosphates which are adsorbed by the soil as anions and thereby produce an increase in the cation-exchange capacity. The smaller the amount of $Ca(OH)_2$ added, the larger is the increase in cation-exchange capacity.

When large amounts of excess $Ca(OH)_2$ are present, a small portion of the added phosphorus is converted by carbonation and equilibration with air into the calcium carbonato-form of the tertiary calcium phosphate and adsorbed by the soil as such.

Some of the $H_2O$-insoluble phosphate retained by the soil may be held in the form of a double layer or a soil micelle-Ca-phosphate linkage.

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*Catalytic Chemistry*. By HENRY WILLIAM LOHSE. Chemical Publishing Company, Inc., Brooklyn, New York, 1945. Pp. 471, figs. 30. Price $8.50.

This book, like Sabatier's *Catalyses in Organic Chemistry*, should be a "catalyst in the study of catalysis." The presentation is factual in an attempt to make the contents as useful as possible to industrial chemists who are concerned with this phase of chemical research. One is impressed from reading the book by the great variety of catalytic reactions and the immense amount of work remaining to be done to develop a really adequate picture of these complicated phenomena. Special attention is directed to the importance of chlorophyll as a catalytic agent in the synthesis of carbohydrates, and to the great variety of other organic catalysts involved in the life processes of plants and animals. The several chapters deal with the history of catalytic chemistry, catalytic theory, the nature and properties of catalysts, specific types of catalytic reactions, and industrial catalytic reaction.

*Food or Famine*. By WARD SHEPPARD. The Macmillan Company, New York, 1945. Pp. 225, plates 16. Price, $3.

Much of the material contained in this book was prepared for use by the National Planning Association of Washington, D. C., but the Association did not sponsor the book. The several chapters contain discussions on erosion, natural and human forces, revolution in soil conservation, forest management, public controls, reconstruction work corps, public acquisition of low-grade land, financing land reconstruction, and integral watershed development. A special plea is made for the development of a more adequate and constructive program for privately owned forestlands, as distinct from the national forests. Specific attention is directed also to the need for a "public conservation works program," but confined to "organized soil or forest conservation districts." Developments of the type of the Tennessee Valley Authority are looked upon with favor, but the need for a "central national coordinating and planning agency" is pointed out to avoid "unbridled and cutthroat regional competition and log-rolling." This is an excellent presentation of the principles involved in the development of an adequate national program of land conservation in terms of human needs.

*Pay Dirt*. By J. I. RODALE. The Devin-Adair Company, New York, 1945. Pp. 242. Price $3.

The purpose of this book is well stated in the following sentences taken from the introduction: "A fertile soil is the foundation of healthy crops, healthy livestock, and last but not least healthy human beings. By a fertile soil is meant one to which Nature's law of return has been faithfully applied, so that it contains an adequate amount of freshly prepared humus made in the form of compost from both vegetable and animal waste." The purpose is to encourage

organic farming, in contrast to the use of fertilizers, weed killers, fungicides, insecticides, and the other "chemical" agents that are now being so widely employed. The book brings together in one volume the concepts of a wide array of believers in Nature's methods, such as Sir Albert Howard, Lady Eve Balfour, Ehrenfreid Pfeiffer, and Thomas J. Barrett, as distinct from those sponsored by the fertilizer industry. It presents the affirmative only.

*Uranium and Atomic Power.* By JACK DE MENT AND H. C. DAKE. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1945. Pp. 343, figs. 12. Price, $4.

The tremendous interest in atomic power arising out of the successful development of the atomic bomb calls for the publication of books of this type at the earliest possible date. The writers of this book have attempted to present the essential information insofar as it is available for their use. The several chapters deal with the occurrence and properties of uranium minerals, their qualitative and quantitative analysis, the chemistry and physics of uranium, and specific methods in uranometry, with very useful bibliographies. The appendixes are of special interest in that they present various constants and properties in relation to this field of research, with a special section on the atomic bomb.

*What Economic System for America?* By CHARLES J. BRAND. Judd and Detweiler, Inc., Washington, D. C., 1945. Pp. 96. Price $1.50.

The burden of this book is the reabsorption of our armed forces into private life and the reconversion of our economic activities from war to peace. The question posed is whether capitalism, economic cooperation, communism, fascism, or national socialism shall prevail. The author discards all coercive systems and advocates a middle-of-the-road course of action "between extreme *laissez faire* on the one hand and excessive governmental intervention and regimentation under bureaucratic domination on the other." The several chapters deal with world resources and population pressures, American diversity of nationalities, races, and religions, and the evidences of our economic progress and social well-being. This is a thoughtful and thought-provoking presentation in very concise form.

THE EDITORS.

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